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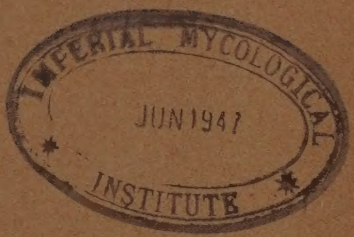

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MATHEMATICS

ON HERMITIAN OPERATORS WHOSE DEFICIENCY INDICES ARE 1

By M. KREIN

(Communicated by S. N. Bernstein, Member of the Academy, 20. XI. 1943)

In this note and in the following ones we intend to expose the main results of a theory, the particular cases of which are the classical results on the problem of moments due to H. Hamburger (1), R. Nevanlinna (2), M. Riesz (3,4), T. Carleman (5) and others; also those of R. Nevanlinna (6) on the interpolation of bounded functions holomorphic within the unit circle, and the results of the author (7) on the problem of continuation of Hermitian-positive functions.

1. Let $\mathfrak{H}$ denote a Hilbert space; A, an Hermitian operator in $\mathfrak{H}$. Thus the domain $\mathfrak{D}_A$ of the operator A is dense in $\mathfrak{H}$, A is closed and $(Ag, f) = (g, Af)\,(g, f \in \mathfrak{D}_A)$.

Denote by $\mathfrak{M}_z$, where z is an arbitrary complex number, the set of elements $\varphi \in \mathfrak{H}$ of form $\varphi = Af - zf$ $(f \in \mathfrak{D}_A)$. As is known, the set $\mathfrak{M}_z$ is closed for any non-real z $(Jz \neq 0)$.

It is easy to see that the intersection $\mathfrak{H}_0$ of all $\mathfrak{M}_z$ reduces the operator A, and A is self-adjoint in $\mathfrak{H}_0$. Furthermore, $\mathfrak{H}_0$ contains every set possessing these properties. Without restricting generality, we may suppose $\mathfrak{H}_0$ to consist of the null element only, *i. e.*

$$\prod_{Jz \neq 0} \mathfrak{M}_z = (0) \tag{1}$$

A one parameter family $E_t\,(-\infty < t < +\infty)$ of bounded self-adjoint operators in $\mathfrak{H}$ will be called spectral function of the operator A if for any $f \in \mathfrak{H}$

1°. $(E_t f, f)$ is a non-decreasing function of t;
2°. $E_t f$ is a left-continuous function of t;
3°. $E_t f \to 0$ as $t \to -\infty$ and $E_t f \to f$ as $t \to \infty$;
4°. for every $f \in \mathfrak{D}_A$

$$(Af, Af) = \int_{-\infty}^{\infty} t^2\, d(E_t f, f), \quad Af = \int_{-\infty}^{\infty} t\, dE_t f \tag{2}$$

If follows from the investigations of M. Neumark (8) that the convergence of the first Stieltjes integral in (2) implies the strong convergence of the second one. By means of the same investigations it is not difficult to show that our definition of the spectral function of an operator coincides with that of Carleman and Stone (5,9).

If for every $t(-\infty<t<+\infty)$ the operator E_t is a projection $(E_t^2=E_t)$, then $E_sE_t=E_{\min(s,\,t)}(-\infty<s,\ t<\infty)$ and the spectral function of the operator A is said to be o r t h o g o n a l.

To every spectral function E_t of the operator A there corresponds a «generalized» resolvent $R_z(Jz\neq 0)$, for which

$$R_zf=\int_{-\infty}^{\infty}\frac{dE_tf}{t-z}\quad(f\in\mathfrak{H},\ Jz\neq 0) \tag{3}$$

If $f\in\mathfrak{M}_z$, then R_zf belongs to $\mathfrak{D}_A$ and does not depend on the choice of the resolvent, being determined by the relation $(A-zE)R_zf=f$.

2. Let us now assume that all deficiency indices of the operator A are equal to 1, *i. e.* the orthogonal complement of $\mathfrak{M}_z$ in $\mathfrak{H}$ is one-dimensional, whenever $Jz\neq 0$.

Let u be a vector in $\mathfrak{H}$ that does not belong to $\mathfrak{M}_z$ for at least one value of z from the upper semi-plane and at least one value from the lower semi-plane.

T h e o r e m 1. *If u is chosen as above, the set E_u of points $\alpha(J\alpha\neq 0)$ such that $u\in\mathfrak{M}_\alpha$ does not possess any non-real limit points and, moreover, the product*

$$\prod_{\alpha\in E}\left|\frac{\alpha+z}{\alpha-z}\right|\quad(Jz\neq 0,\quad z\overline{\in}E_u)$$

converges.

Let us fix such an element u; it will be called a s c a l e in the following.

T h e o r e m 2. *To every element $f\in\mathfrak{H}$ there corresponds a function $f_u(z)$ $(Jz\neq 0)$ such that its only singularities in the semi-planes $Jz>0$ and $Jz<0$ are poles belonging to the set E_u and $f-f_u(z)u\in\mathfrak{M}_z$ whenever $f_u(z)\neq\infty$ $(Jz\neq 0)$.*

3. Denote by $\mathfrak{H}_u$ the totality of all functions $f_u(z)\,(f\in\mathfrak{H})$.

T h e o r e m 3. *The correspondence $f\to f_u(z)$ is a one-to-one linear correspondence between $\mathfrak{H}$ and $\mathfrak{H}_u$ such that $u\to 1$ and $g=Af$ $(f\in\mathfrak{D}_A)$ implies $g_u(z)=zf_u(z)$.*

4. Denote by V_u the totality of non-decreasing functions $\sigma(t)\,(-\infty<t<\infty)$ generated by the spectral functions E_t of the operator A: $\sigma(t)=(E_tu,\ u)$ $(-\infty<t<\infty)$. Evidently,

$$\sigma(t)=\sigma(t-0)\ (-\infty<t<\infty),\ \sigma(-\infty)=0,\ \sigma(\infty)=(u,\ u).$$

T h e o r e m 4. *Two spectral functions E_t of the operator A coincide if and only if the corresponding functions $\sigma\in V_u$ are equal.*

A function $\sigma\in V_u$ will be called c a n o n i c a l if it is generated by an orthogonal spectral function of the operator A.

It is known that a real function $\sigma(t)$ of bounded variation such that $\sigma(t)=\sigma(t-0)$ $(\sigma(-\infty)=0)$ is completely determined by the integral

$$w_\sigma(z)=\int_{-\infty}^{\infty}\frac{d\sigma(t)}{t-z}\quad(Jz>0) \tag{4}$$

Below we shall find the general form of the functions $w_\sigma(z)$ corresponding to the functions $\sigma(t)=(E_tu,\ u)\in V_u$; note that in this case [see (3)]

$$w_\sigma(z)=(R_zu,\ u) \tag{5}$$

5. From the condition (1) and the assumption that all deficiency indices of the operator A are equal to 1 it readily follows that the space $\mathfrak{H}$ is separable.

Let $\{\varphi_k\}$ be an orthonormalized complete system of elements in $\mathfrak{H}$. Put for brevity

$$\varphi_{ku}(z) = \varphi_k(z) \qquad (z = 1, 2, \ldots)$$

As $\varphi_k - \varphi_k(z)\, u \in \mathfrak{M}_z$ $(k = 1, 2, \ldots)$, the element $R_z[\varphi_k - \varphi_k(z)\, u]$ and, consequently, the expressions

$$\psi_k(z) = (R_z[\varphi_k - \varphi_k(z)\, u],\ u) \quad (k = 1, 2, \ldots)$$

do not depend on the choice of the generalized resolvent of the operator A.

It is obvious that $\psi_k(z)$ $(Jz \neq 0,\ k = 1, 2, \ldots)$ are meromorphic functions in the interior of the semi-planes $Jz > 0$, $Jz < 0$, whose poles belong to the set E_u.

Whatever be a function $\varphi(z)$, let us denote $\overline{\varphi(\bar{z})}$ simply by $\bar{\varphi}(z)$.

Theorem 5. *For any z $(Jz \neq 0)$ the set of points $w_\sigma(z)$ $(\sigma \in V_u)$ fills a circle $C(z)$ lying within the same semi-plane as the point z. This circle is reduced to a point if and only if $z \in E_u$. The centre $\zeta(z)$ and the radius $r(z)$ of the circle $C(z)$ are determined by the formulae*

$$\left.\begin{aligned} \zeta(z) &= \frac{i - 2y \sum_1^\infty \overline{\varphi_k(z)}\, \psi_k(z)}{2y \sum_1^\infty |\varphi_k(z)|^2} \\ r(z) &= \frac{1}{2y \left[\sum_1^\infty |\varphi_k(z)|^2 \sum_1^\infty |\varphi_k(\bar{z})|^2\right]^{1/2}} \end{aligned}\right\} \tag{6}$$

The equation of the boundary of $C(z)$ in the w-plane can be represented in the form

$$\frac{w - \bar{w}}{z - \bar{z}} = \sum_1^\infty |w\varphi_k(z) + \psi_k(z)|^2 \tag{7}$$

The point $w_\sigma(z)$ belongs to the boundary of the circle $C(z)$ if and only if $\sigma \in V_u$ is a canonical function; in this case the canonical function corresponding to any point w of the boundary of $C(z)$ is unique.

This theorem is connected closely with the following

Theorem 6. *The boundary of the circle $C(z)$ $(Jz \neq 0)$ can be determined by the following parametric equation*

$$w = \frac{p_0(z) + \tau p_1(z)}{q_0(z) + \tau q_1(z)} \quad (-\infty \leqslant \tau \leqslant \infty) \tag{8}$$

where $q_i(z)$, $p_i(z)$ $(i = 0, 1)$ are meromorphic functions within the upper and the lower semi-planes, whose poles belong to the set E_u; they are connected with the functions $\varphi_k(z)$ and $\psi_k(z)$ $(k = 1, 2, \ldots)$ by the following relations:

$$\left.\begin{aligned} q_0(z)\,\overline{q_1(\zeta)} - q_1(z)\,\overline{q_0(\zeta)} &= (z - \bar{\zeta}) \sum_1^\infty \varphi_k(z)\,\overline{\varphi_k(\zeta)}, \\ p_0(z)\,\overline{p_1(\zeta)} - p_1(z)\,\overline{p_0(\zeta)} &= (z - \bar{\zeta}) \sum_1^\infty \psi_k(z)\,\overline{\psi_k(\zeta)} \\ q_0(z)\,\overline{p_1(\zeta)} - q_1(z)\,\overline{p_0(\zeta)} &= 1 + (z - \bar{\zeta}) \sum_1^\infty \varphi_k(z)\,\overline{\psi_k(\zeta)}, \end{aligned}\right\} \tag{9}$$

where z and ζ are arbitrary non-real points not contained in the set E_u.

It is not difficult to show that the relations (9) determine the functions $q_i(z)$, $p_i(z)$ $(i=0, 1)$ completely up to linear transformations

$$p_0^*(z)=e^{i\theta}(\alpha p_0(z)+\beta p_1(z)), \quad q_0^*(z)=e^{i\theta}(\alpha q_0(z)+\beta q_1(z))$$
$$p_1^*(z)=e^{i\theta}(\gamma p_0(z)+\delta p_1(z)), \quad q_1^*(z)=e^{i\theta}(\gamma q_0(z)+\delta q_1(z))$$

where $0\leqslant\theta<2\pi$ and α, β, γ, δ are any real numbers such that $\alpha\delta-\beta\delta=1$.

If all $\varphi_k(z)$ $(k=1, 2, \ldots)$ are holomorphic in a neighbourhood of a real point ξ, then [see ([10]), Theorem 15] the same is true of the functions $\psi_k(z)$ $(k=1, 2, \ldots)$ and the functions $q_i(z)$, $p_i(z)$ $(i=0, 1)$ can be represented by the formulae:

$$q_0(z)=1-(z-\xi)\sum_1^\infty \overline{\psi_k(\xi)}\,\varphi_k(z), \quad q_1(z)=-(z-\xi)\sum_1^\infty \overline{\varphi_k(\xi)}\,\varphi_k(z)$$

$$p_0(z)=(z-\xi)\sum_1^\infty \overline{\psi_k(\xi)}\,\varphi_k(z), \qquad p_1(z)=1+(z-\xi)\sum_1^\infty \overline{\varphi_k(\xi)}\,\psi_k(z)$$

Theorem 7. *To every function $\tau(z)$ holomorphic within the upper semi-plane satisfying the condition*

$$J\tau(z)\geqslant 0 \quad (Jz>0)$$

as well as to function $\tau(z)\equiv\infty$ there corresponds one and only one non-decreasing bounded function $\sigma(t)=\sigma(t-0)$ $(-\infty<t<\infty$, $\sigma(-\infty)=0)$ such that

$$\frac{p_0(z)+\tau(z)\,p_1(z)}{q_0(z)+\tau(z)\,q_1(z)}=\int_{-\infty}^{\infty}\frac{d\sigma(t)}{t-z} \tag{10}$$

The set of functions $\sigma(t)$ so obtained coincides with the set V_u.*

It follows from this theorem that a non-decreasing bounded function $\sigma(t)=\sigma(t-0)$ $(-\infty<t<\infty$, $\sigma(-\infty)=0)$ belongs to V_u if and only if the point $w_\sigma(z)$ is contained in the circle $C(z)$ for every z $(Jz>0)$.

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* When the manuscript was ready for publication the author came to know that M. Neumark ([10]) had obtained a result analogous to Theorem 7.

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ASTRONOMY

ON THE «ELLIPTICITY» OF THE EARTH'S EQUATOR

By A. J. ORLOV, Corresponding Member of the Academy

In the case of the three-axial ellipsoid of inertia of the Earth the path of free nutation of the pole with Chandler's period $T=1.2$ should be an ellipse, whose minor axis coincides in direction with the major equatorial axis of the ellipsoid of inertia (1). It is evident that the excentricity of this ellipse is very small and its determination is all the more difficult, because the free nutation is always accompanied by an annual wave. Moreover, the amplitudes and phases of these two components of the motion of the pole do not remain constant, and their separation is impossible unless based upon a great number of observations.

At the present time the coordinates of the pole are known for a period of about fifty years, and many attempts have been made to determine the ellipticity of Chandler's pole motion. However, the data available are insufficient to evaluate the probable error of the result.

Denote by x_t and y_t the coordinates (2) of the instantaneous pole at the moment t, and suppose that

$$x_t = A\cos(\mu t+\alpha)+\text{annual term}$$
$$y_t = B\cos(\mu t+\beta)+\text{annual term}$$

Here $\mu=\frac{2\pi}{T}$, where T is Chandler's period. The time t we express in years.

To exclude the annual term, we take the differences $x_c=x_{t+1}-x_t$, $y_c=y_{t+1}-y_t$. Suppose $T=1.2$, then x_c and y_c are the coordinates of the pole at the moment $t=+0.8$, if there is only one free nutation. Now the x_c and y_c must be arranged according to the same phases of the argument μt. For this purpose we must, first, determine the precise value of the period T. To do this, we begin with the supposition that the pole moves regularly on a circle with the period $T=1.2$; then x_c for moment $t=+0.3$ must be equal to y_c for moment t. This being assumed, we take the half-sums

$$S=\frac{(x_c)_{t+0.3}+(y_c)_t}{2}$$

and represent each of the twelve consecutive values of S by the formula

$$S=C\cos(300^\circ t\mp\gamma)$$

The values of C and γ obtained in this manner are given in the third and fourth columns of the table here adjoined. The continuous increase of γ shows that the period assumed is somewhat too great. As γ increases till 1925 for each period of 1.2 years approximately by 3°, a more precise value of T is 1.19, thus $\mu=302^\circ.5$. The initial phase for 1892.3, calculated from $\gamma_0=\gamma+3^\circ k$, where k is the number of periods, is given in the last column of the table. We see that in 1925 Chandler's motion of the pole changed radically. For the determination of A, B, α

and β we use only the data from 1892.3 till 1924.6. As an average we obtain $x_c = 0.''146 \cos(302°.5t + 167°.2)$, $y_c = 0''.151 \cos(302°.5t + 256°.3)$, the time being counted from 1892.3.

k	Date	C in 0.″01	γ	γ_0	k	Date	C in 0.″01	γ	γ_0
0	1892.3	15	262	262	20	1916.3	11	307	247
1	93.5	14	260	257	21	17.5	12	314	251
2	94.7	11	265	259	22	18.7	15	323	257
3	95.9	16	269	260	23	19.9	14	306	237
4	97.1	15	254	242	24	1921.1	6	321	249
5	98.3	12	255	240	25	22.3	10	348	273
6	99.5	11	266	248	26	23.5	10	334	256
7	1900.7	14	271	250	27	24.7	6	316	235
8	01.9	12	271	247	28	25.9	4	100	16
9	03.1	12	276	249	29	27.1	4	49	322
10	04.3	12	286	256	30	28.3	4	159	69
11	05.5	9	294	261	31	29.5	7	133	40
12	06.7	15	327	291	32	1930.7	5	173	77
13	07.9	22	321	282	33	31.9	8	166	67
14	09.1	25	312	270	34	33.1	5	182	80
15	1910.3	23	315	270	35	34.3	8	199	94
16	11.5	24	310	262	36	35.5	6	187	79
17	12.7	22	309	258	37	36.7	4	202	91
18	13.9	18	304	250	38	37.9	5	208	94
19	15.1	18	306	249					

The amplitudes of x_c and y_c are nearly equal and the initial phases differ but quite insensibly from 90°. Thus, the pole motion due to the free nutation may be looked upon as a circular one, and further calculations seem to be needless. If nevertheless we suppose the motion to be elliptical and carry out the corresponding calculations to the end, we shall receive for the direction of the major axis of the ellipse 78°, and consequently for the direction of the major axis of the Earth's equator 12° E.

Geodetic and gravimetric measurements have led in the mean to exactly the same conclusion. So close an agreement may hardly be believed to be merely a chance coincidence.

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13. III. 1944.

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PHYSICS

A NEW METHOD FOR ACCELERATION OF RELATIVISTIC PARTICLES

By V. I. VEKSLER

(Communicated by N. D. Papalexi, Member of the Academy, 25. IV. 1944)

It is believed that the method of resonance acceleration which has been carried into effect by Lawrence (1) for heavy particles (cyclotron) cannot be used for the acceleration of electrons, because the mass of the particles is relativistically variable with the velocity. This difficulty is circumvented in the accelerator with vortex-field, suggested by Wideröe (2) and which Kerst (3) has been the first to materialize. In Kerst's apparatus as high energies of the electron beam as 20 MeV have already been attained, and it appears that particles with an energy approaching 100 MeV will shortly be available. However, further increase of the electron energy by Kerst's method is fraught with great technical difficulties.

It seems therefore advisable to point out a new possibility of obtaining relativistic particles, based upon a simple generalization of the resonance method.

Principle of Operation of the Accelerator. That it is possible in principle to obtain very fast relativistic particles by the resonance method will become evident, if we consider the simplest case where a charged relativistic particle is moving in a resonance accelerator, *i. e.* in a system consisting in the general case of N accelerating intervals* lying on a circumference, and a magnetic field invariable with time and directed at right angles to the plane of the duants. Denote by ν the frequency of an alternating field applied to the duants (period T_λ) and by V_0 (volts), the amplitude. If the magnitude of the magnetic field is H_0, then the time of travel of a particle along the circumference is known to be

$$T = \frac{2\pi mc}{H_0 e}$$

where $m = \frac{m_0}{\sqrt{1-\beta^2}}$; e, charge; c, the velocity of light.

Express the mass of the particle m as a function of its full energy. Then the time of travel T_n/N in the accelerating interval along the $1/N$ portion of the circumference after it has been passed n times will be

$$\frac{T_n}{N} = \frac{2\pi\,(enV_0 + m_0c^2)}{NeH_0c} \qquad (1)$$

As long as $enV_0 \ll m_0c^2$, one may assume that $T_n = T_{n-1} = T_0 = \text{const}$. And it is just this case that is turned to account in the cyclotron for the acceleration of protons.

It will be obvious that in the case of electrons, T_n cannot possibly be regarded as constant even for small energies. It is easy to show, however, that the

* In cyclotron $N = 2$.

increase of T_n with increasing energy of the particles is no barrier to the use of the resonance method for the acceleration of particles. This statement becomes at once apparent, if one determines the time difference between the T_{n+1}-th and T_n-th revolution. For simplicity sake we confine ourselves to the case where $N=1$*.

$$T_{n+1} - T_n = \frac{2\pi V_0}{H_0 c} = \Delta T \qquad (2)$$

Then formula (2) shows that the time difference between two successive cycles is a constant quantity independent of the full energy of the particle, *i. e.* of n. This circumstance does not appear to have been given due attention so far. Yet it opens the possibility for the acceleration of relativistic particles by the resonance method.

Let us so choose the constants V_0 and H_0 that

$$T_{n+1} - T_n = \frac{2\pi V_R}{H_R c} = T_\lambda \qquad (3)$$

If at the same time we impose the initial condition

$$T_1 = T_\lambda + \frac{2\pi m_0 c\,(k+1)}{H_R e} = T_\lambda \gamma \qquad (4)$$

where T_λ is the period of oscillation; $k = eV_i/m_0c^2$; V_i is the potential difference, corresponding to the initial velocity of the particle previous to first acceleration; γ is an arbitrary integer, then the particle will be in resonance with the field, in spite of the fact that the time of its travel along the circumference increases after each acceleration.

In physical terms this will mean that after every acceleration the time of travel of the particle along the circumference increases just by the value of the period. Therefore as the energy of the particle grows, the latter will fall farther and farther behind the field in phase. In every new revolution, however, this lagging will be equal to a whole period (if $N \geqslant 2$), so that the particle will gain speed continuously.

Formulae (3) and (4) give all that is necessary for the design of such an accelerator. Combining (3) and (4) we can obtain

$$V_R = \frac{m_0 c^2 (k+1)}{e\,(\gamma-1)}; \quad H_R = \frac{m_0 c\,(k+1)\,2\pi}{eT_\lambda\,(\gamma-1)}$$

At the exit the energy (in volts) is

$$E = \frac{300 \cdot 2\pi m_0 c\,(k+1)}{eT_\lambda\,(\gamma-1)}\,\rho_k$$

where ρ_k is a finite radius.

It will be apparent that a very simple generalization of the resonance method** makes it suitable (at least in principle) for the acceleration of relativistic particles and production of arbitrarily high energies.

It is well to point out a very important feature by which any resonance accelerator is distinguished, which for the acceleration of particles takes advantage of the fact that the increment of the time of a revolution is a constant quantity. In this case, unlike that of the ordinary cyclotron, a strictly definite value (in

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* This may be achieved, for instance, by using an endovibrator.

** It should be emphasized that the author has deliberately confined himself to the consideration of a simple and well-known scheme of a resonance accelerator in order to bring out the more clearly the chief idea of the method he suggests. Its realization, however, is possible, at least in principle, in many other ways.

absolute magnitude) of the acceleration potential difference is necessary for the resonance. It is easy to show that if the amplitude of the field V is larger than the resonance amplitude, the particles will by themselves be in phase at the resonance point $V = V_R$, or, in other words, the resonance is stable. To make it clear we shall revert to the discussed instance of accelerator supplied with an endovibrator. From formulae (3) and (4) it may be seen that stability actually takes place in such an accelerator**. If the potential difference accelerating the particles is slightly decreased upon the n-th acceleration, the result is that for the $n+1$ time the particles approach the accelerating interval somewhat earlier than after $2T_\lambda$, and so get into a field that is somewhat stronger than that which imparted them acceleration the last time. Contrary to this, if upon the n-th revolution the particles reach the accelerator at a V somewhat larger than V_R, they will lag farther behind than by $2T_\lambda$ and, when accelerated for the $n+1$ time, will pass across a weaker field than they did during the n-th acceleration.

These automatically established relations are due to the fact that the interval of time between two successive accelerations depends upon the accelerating potential difference. This is a general property of all accelerators of this type, and owing to it the acceleration can (at least in principle) be materialized by a variety of methods, even if the magnetic field should increase with time.

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** Stable is the point $V = V_R$, which corresponds to the second quarter of the half-period, when the potential difference in the accelerating interval decreases with time.

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PHYSICS

ELECTRO-OPTICAL PROPERTIES OF VALENCE OSCILLATIONS

By M. W. WOLKENSTEIN

(Communicated by S. I. Wawilow, Member of the Academy, 25. II. 1944)

Of late the author has discussed the polarization properties of the deformation oscillations in Raman spectra of polyatomic molecules (2). This he did within the scope of the zero approximation theory based upon an optical valence scheme (1). Now he will turn to the valence oscillations.

Let us consider the practically interesting case of a group of n similar σ-bonds forming similar angles with one another (*e. g.*, CH, CH_2, CH_3, CH_4). We will compute the degree of depolarization and the intensity of a completely symmetrical valence oscillation of this group as functions of n and γ. While doing so we regard the oscillations as purely valent, or, in other words, assume that the bond angles are not affected by the oscillations.

The valence part of the tensor $\frac{\partial b_{ik}}{\partial Q}$ has the form (1)

$$\left(\frac{\partial b_{ik}}{\partial Q}\right)_\gamma = \sum_n \left\{ \left(\frac{\partial \alpha_{n1}}{\partial q_n} - \frac{\partial \alpha_{n2}}{\partial q_n} \right) \cos(ni) \cos(nk) + \frac{\partial \alpha_{n2}}{\partial q_n} \delta_{ik} \right\} \frac{\partial q_n}{\partial Q} \qquad (1)$$

where n is the bond number; α_{n1} [α_{n2}], polarizability along [across] the σ-bond; $\cos(ni)$, directing cosine of the n-th bond with respect to axis i.

Let us compute the spur and anisotropy of the tensor (1) taking it for granted that all $\alpha_{n1} = \alpha_1$, and $\alpha_{n2} = \alpha_2$, and also that all bonds form similar angles γ with each other. For completely symmetrical oscillations all $\frac{\partial q_n}{\partial Q}$ are equal, too

$$\frac{\partial q_n}{\partial Q} = \frac{\partial q}{\partial Q} = \frac{\omega}{\sqrt{nk}} \qquad (2)$$

where ω is the frequency of oscillation, and k, the dynamic coefficient of the q-bond.

We have the spur of (2)

$$A_n = \sum_i \left(\frac{\partial b_{ii}}{\partial Q}\right)_\gamma = \frac{\partial q}{\partial Q} n \left(\frac{\partial \alpha_1}{\partial q} + 2 \frac{\partial \alpha_2}{\partial q} \right) = \sqrt{n} \frac{\omega_n}{\omega_1} A_1 \qquad (3)$$

the square of the anisotropy of (2)

$$B_n^2 = \frac{3}{2} \sum_{i,k} \left(\frac{\partial b_{ik}}{\partial Q}\right)_\gamma^2 - \frac{1}{2} \left(\sum_i \left(\frac{\partial b_{ii}}{\partial Q}\right)_\gamma \right)^2 =$$

$$= \left(\frac{\partial q}{\partial Q}\right)^2 n^2 \left(\frac{\partial \alpha_1}{\partial q} - \frac{\partial \alpha_2}{\partial q} \right)^2 \left(1 - \frac{n-1}{2n} 3 \sin^2 \gamma \right) = n \frac{\omega_n^2}{\omega_1^2} B_1^2 \left(1 - \frac{n-1}{2n} 3 \sin^2 \gamma \right) \qquad (4)$$

where $A_1 = \alpha_1' + 2\alpha_2'$ and $B_1 = \alpha_1' - \alpha_2'$ are the spur and anisotropy for a single σ-bond.

The degree of depolarization

$$\rho_n = \frac{6B_1^2\left(1 - \frac{n-1}{2n}3\sin^2\gamma\right)}{5A_1^2 + 7B_1^2\left(1 - \frac{n-1}{2n}3\sin^2\gamma\right)} \tag{5}$$

falls off rapidly with increasing n, whereas the intensity grows (in the case of small variation of oscillation frequencies)

$$I_n \sim nf\left\{5A_1^2 + 13B_1^2\left(1 - \frac{n-1}{2n}3\sin^2\gamma\right)\right\} \tag{6}$$

where

$$f = \frac{(\omega_n - \omega_0)^4}{\omega_n}\,\frac{1}{1 - \exp\left(-\frac{\hbar\omega}{kT}\right)}\,\frac{\omega_n^2}{\omega_1^2}$$

In the table the computed values of ρ refer to symmetrical C—H valence oscillations in bromo-methanes [3]. A_1 and B_1 have been found from chloro-methane spectra.

	ω, cm^{-1}	ρ_n (5)	ρ_n [3]	ρ_n experim.
CH_4	2914	0	0	(0)
CH_3Br . . .	2973	0.05	0.05	0.10
CH_2Br_2 . .	2988	0.13	0.11	0.10
$CHBr_3$ . . .	3021	0.31	0.22	0.25

The values obtained in the previous work [3] are more accurate, because then the share of the deformation was taken into account. Nevertheless, the formulae (5) and (6) afford the means for a direct inquiry into symmetric valence oscillations. These oscillations are particularly intense and, being apt to display some typical mechanical and electro-optical properties, are much the most essential in the analysis of structure. Besides, the relation (5) permits the shape of the ellipsoid $\partial\alpha/\partial q$ to be estimated directly.

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OCEANOLOGY

GEOMETRICAL PROPERTIES OF ϑ, s-CURVES ON THE MIXING OF THREE WATER MASSES IN UNLIMITED SEA

By W. B. STOCKMAN

(Communicated by P. P. Shirshov, Member of the Academy, 26. X. 1943)

By water masses of a sea or ocean we mean, according to Defant (1), such homogeneous water volumes, limited or unlimited, as are characterized by definite physical and chemical properties, for instance, the temperature of water ϑ, or its salinity, s.

In studying the mixing of water masses in sea-faring practice the Helland-Hansen (2) method of ϑ, s-diagrams has found a wide application. The essence of this method is that the different depths of a given vertical section of the sea are plotted in a rectangular system of coordinates ϑ, s against temperature ϑ and salinity s. In this representation salinity is a function of temperature ϑ and parameters z (depth) and t (time). The lines of the diagram corresponding to a constant value of the parameter t are called ϑ, s-curves.

Until recently the method of ϑ, s-curves was mainly of a purely descriptive qualitative character, but not long ago we were able to build an analytical theory of this method and to formulate a set of theorems that made the basis of a «geometry of ϑ, s-curves». These theorems have important practical implication.

On account of the space available, I restrict the discussion to the main geometrical properties of ϑ, s-curves when three water masses are mixed in an unlimited sea. The other results of my study will be published elsewhere.

Let us examine the case of a vertical mixing of three water masses of which one, the intermediate, is limited. Place the origin of the vertical coordinate ($z=0$) in the centre of the intermediate water mass whose boundaries correspond to the values $z=\pm h$. The two other masses extend to infinity—from $z=h$ to $z=\infty$ and from $z=-h$ to $z=-\infty$. The temperature and salinity of the water masses at the initial instant $t=0$ are

$$\left.\begin{array}{ll} \text{I)} & \vartheta=\theta_1, \quad s=S_1 \quad (\infty > z > h) \\ \text{II)} & \vartheta=\theta_2, \quad s=S_2 \quad (h > z > -h) \\ \text{III)} & \vartheta=\theta_3, \quad s=S_3 \quad (-h > z > -\infty) \end{array}\right\} \tag{1}$$

Suppose the coefficient of the turbulent mixing k in the region of the three water masses to be invariable. Then the process of mixing can be described by differential equations of the Fourier type:

$$\frac{\partial \vartheta}{\partial t}=k\frac{\partial^2 \vartheta}{\partial z^2}, \quad \frac{\partial s}{\partial t}=k\frac{\partial^2 s}{\partial z^2} \tag{2}$$

whose solution has the form

$$\vartheta=\frac{1}{2\sqrt{\pi k t}}\int_{-\infty}^{+\infty} F(\xi)\, e^{-\frac{(\xi-z)^2}{4kt}}\, d\xi \tag{3}$$

$$s=\frac{1}{2\sqrt{\pi k t}}\int_{-\infty}^{+\infty} f(\eta)\, e^{-\frac{(\eta-z)^2}{4kt}}\, d\eta \tag{3'}$$

where $F(\xi)$ and $f(\eta)$ are the initial distribution of temperature and salinity which may be either of continuous or broken character.

If now the initial distribution according to (1) is substituted in (3) and (3′) for $F(\xi)$ and $f(\eta)$, we shall after some transformations obtain the following formulae for the temperature

$$\left.\begin{aligned}
&\text{I)}\ \vartheta = \frac{1}{2}\left[\theta_1+\theta_3+(\theta_1-\theta_2)\,\Phi\left(\frac{z-h}{2\sqrt{kt}}\right)+\right.\\
&\left.+(\theta_2-\theta_3)\,\Phi\left(\frac{z+h}{2\sqrt{kt}}\right)\right]\quad(\infty>z>h)\\
&\text{II)}\ \vartheta = \frac{1}{2}\left[\theta_1+\theta_3-(\theta_1-\theta_2)\,\Phi\left(-\frac{z-h}{2\sqrt{kt}}\right)+\right.\\
&\left.+(\theta_2-\theta_3)\,\Phi\left(\frac{z+h}{2\sqrt{kt}}\right)\right]\quad(h>z>-h)\\
&\text{III)}\ \vartheta = \frac{1}{2}\left[\theta_1+\theta_3-(\theta_1-\theta_2)\,\Phi\left(-\frac{z-h}{2\sqrt{kt}}\right)-\right.\\
&\left.-(\theta_2-\theta_3)\,\Phi\left(-\frac{z+h}{2\sqrt{kt}}\right)\right](-h>z>-\infty).
\end{aligned}\right\}\qquad(4)$$

and the corresponding formulae for the salinity. In formulae (4)

$$\Phi(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-\eta^2}\,d\eta$$

is the integral of errors.

It should be remarked that the three water masses I, II and III are represented in the ϑ, s-diagram at the initial moment of mixing by three points forming a certain «triangle of mixing». This is a fundamental concept for the whole theory of ϑ, s-curves.

The side I—III will be defined as the b a s e of this mixing triangle. From the formulae for ϑ and s of type (4) there arises a series of consequences concerning the geometrical properties of ϑ, s-curves.

T h e o r e m 1. *The locus of points with $z=0$ characterizing the transformation of the core of the intermediate water mass is the «main» median of the mixing triangle, drawn from that of its apices which corresponds to the intermediate water mass.*

T h e o r e m 2. *At the initial moment of mixing the ϑ, s-curve is a broken line composed of two straight lines connecting successively the water masses* I—II, II—III.

T h e o r e m 3. *The branches of the ϑ, s-curves at a sufficient distance from the boundaries of the intermediate water mass touch the straight lines connecting the water masses at the initial stage of mixing.*

T h e o r e m 4. *The points of ϑ, s-curves corresponding to the parameter $z=0$ are points of the extremum of the ϑ, s-curves with respect to the base of the mixing triangle.*

T h e o r e m 5. *The straight lines connecting two such points of the ϑ, s-curve for which the parameter z takes values equal in magnitude but opposite in sign, run parallel to the base of the mixing triangle.*

T h e o r e m 6. *The tangent to a given ϑ, s-curve at the point corresponding to $z=0$ cuts another ϑ, s-curve, preceding the former in time, at two points for which the values of the parameter z are equal but opposite in sign.*

T h e o r e m 7. *All points corresponding in the system $s=f(\vartheta)$ to the boundaries of the intermediate layer of water lie on the straight lines connecting the median points of the two respective lateral sides of the mixing triangle with the median point of its base. On the ϑ, s-curves these «collateral median lines» of the mixing triangle cut off arcs that characterize the water of the intermediate layer in the system $s=f(\vartheta)$.*

Fig. 1 is a graphic illustration to these theorems. The parallelogram II ABC characterizes in the system $s=f(\vartheta)$ (in accordance with Theorem 7) the transformation of water of the intermediate layer.

By means of the Theorems 3 and 7 we can not merely restore the initial thermohaline indices ϑ, s of the water masses, but also determine the thickness of the intermediate water layer at the initial stage of mixing. To do so we must build the mixing triangle and then draw its collateral medians AB and BC (Fig. 1).

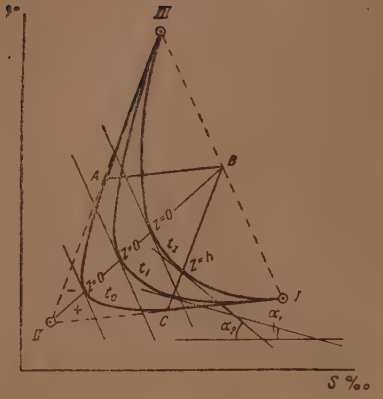

Fig. 1

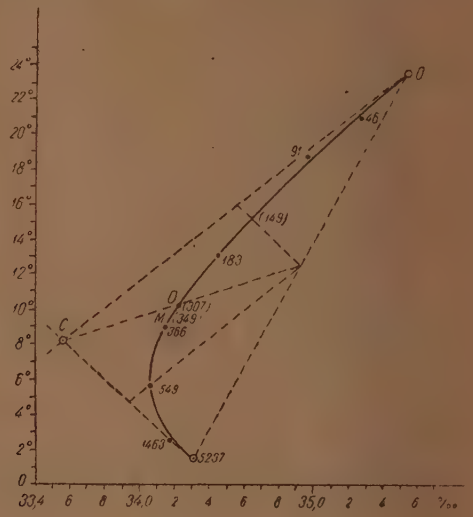

Fig. 2

If we now determine the depth of the intersection points of the collateral medians with the given ϑ, s-curve, we shall find the sought-for boundaries of the intermediate layer.

In Fig. 2 a ϑ, s-curve, as plotted by G. Wüst (3), represents the vertical distribution of temperature and salinity in the central part of the Pacific ($\varphi=33°22'$ N; $\lambda=154°56'$ W). The necessary constructions are shown in the same figure. It is seen that the collateral medians of the mixing triangle cross the ϑ, s-curve at the points where $z=549$ m and $z=149$ m (the latter value has been found by interpolation). The depth established in this simple way corresponds to the sought-for boundaries of the intermediate layer of «subarctic water».

Up to this date the judgments of sea-farers as to the vertical boundaries of some particular layer in the sea have been rather vague and arbitrary. This is because the vertical distribution of the different properties of sea water bears a continuous character, owing to the equalizing effect of the mixing processes. But the difficulties can easily be removed by means of Theorem 7.

Let us see how propositions proved by us stand their ground under real conditions. According to our theorems, the point O, at which the main median line of the mixing triangle crosses the empirical curve of Fig. 2, should be equidistant (with respect to depth z) from the intersection points of this curve with the collateral medians of the triangle.

In Fig. 2 a depth of 307 m corresponds to the point O, while the point M with $z=349$ m corresponds to the middle of the intermediate layer. So there is no considerable divergence between the depths at points O and M, and the relative error (referred to the thickness of the intermediate layer, 400 m) is only 12 per cent.

It is obvious that the propositions on which we have based our estimation of the thickness of the intermediate layer meet the conditions prevailing in the Pacific with sufficient accuracy (exactly they may be fulfilled only in a sea of infinite depth).

To conclude I will show a simple graphic method for the calculation of another unknown parameter of the ϑ, s-curve, *viz.* the magnitude of the mixing coefficient k. It follows from the formulae of type (4) that the lines touching the curve at the points corresponding to the boundary of the intermediate layer have the tangents of their inclination angles determined for the instants t_1 and t_2 by the expressions

$$\operatorname{tg}\alpha_1 = \frac{\theta_1 - \theta_2 + (\theta_2 - \theta_3)\, e^{\frac{h^2}{kt_1}}}{S_1 - S_2 + (S_2 - S_3)\, e^{\frac{h^2}{kt_1}}}; \quad \operatorname{tg}\alpha_2 = \frac{\theta_1 - \theta_2 + (\theta_2 - \theta_3)\, e^{\frac{h^2}{kt_2}}}{S_1 - S_2 + (S_2 - S_3)\, e^{\frac{h^2}{kt_2}}}$$

whence

$$e^{\frac{h^2}{kt_1}} = A; \quad e^{\frac{h^2}{kt_2}} = B. \tag{5}$$

where

$$A = \frac{\theta_1 - \theta_2 - (S_1 - S_2)\operatorname{tg}\alpha_1}{(S_2 - S_3)\operatorname{tg}\alpha_1 - \theta_2 + \theta_3}; \quad B = \frac{\theta_1 - \theta_2 + (S_1 - S_2)\operatorname{tg}\alpha_2}{(S_2 - S_3)\operatorname{tg}\alpha_2 - \theta_2 + \theta_3}.$$

Taking logarithms of (5) and composing the difference $t_2 - t_1 = \Delta t$, we get

$$k = \frac{(z'' - z')^2}{4\Delta t} \frac{\ln B - \ln A}{\ln B \ln A} = \frac{(z'' - z')^2}{4\Delta t} M \tag{6}$$

where $z'' - z'$ is the difference between the depths cut off on the ϑ, s-curve by the collateral medians of the mixing triangle.

It is interesting to note that formula (6) bears a certain resemblance to Jacobsen's formula (4), though the quantities $z'' - z'$ in these two formulae have by no means the same sense.

In practice the factor M of formula (6) is determined as follows. One draws tangents at the intersection points of the collateral median with two ϑ, s-curves, succeeding each other in time, as is shown in Fig. 1, and then determines the angles formed by these tangents with the axis s.

Upon the theory of ϑ, s-curves, as set forth here, we may put an interesting hydrodynamic interpretation. If, indeed, we consider a plane-parallel motion of an unlimited viscous incompressible fluid in the absence of external forces, the Navier-Stokes equations can be reduced to the form

$$\frac{\partial u}{\partial t} = \nu \frac{\partial^2 u}{\partial z^2}; \quad \frac{\partial v}{\partial t} = \nu \frac{\partial^2 v}{\partial z^2} \tag{7}$$

and become formally analogous to equations (2). In (7) u and v are components of the horizontal vector of the velocity along the axes x and y; ν is coefficient of kinematic viscosity. It is easy to realize that in the case of the motion described by equations (7) the ϑ, s-curve has its analogue in the flow velocity curves whose equation has the form $u = f(v, z, t)$. It is evident also that the vertices of the mixing triangle correspond to the ends of three vectors (drawn from the origin) representing the velocity distribution at the initial moment.

Thus, in the special case of a flow of viscous incompressible fluid, the velocity curves have all of the geometric properties discovered by us in ϑ, s-curves, and the value of the kinematic coefficient of viscosity may be determined from (6).

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BIOPHYSICS

RESOLVING POWER OF UNAIDED AND ARMED EYE

By D. MAKSUTOV

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In our previous note (1) we treated some problems of the theory of image formation on the retina.

The present article is concerned with the observation and resolution of a double star by an unaided and an armed eye with different diameter of the pupil and of the exit pupil of the instrument. Empirical formulae are also given for the upper angular limit of resolution for visual optical apparatus.

All the results apply to the author's right eye.

§ 1. Resolving Power of the Unaided Eye. If the eye were an ideal optical instrument, it would resolve with $\lambda = 0.555\ \mu$ a double star with a distance between the components p_T seconds of arc

$$p_T = \frac{114}{d_T} (\text{sec. of arc}) \qquad (1)$$

this being the theoretical limit of resolution, as deduced from the diffraction theory of image formation, the contrast sensitivity of the eye being taken into account.

However, the eye does not resolve such a small angle, because of its optical imperfection, mainly because of the heterogeneity of the lens. The front of the wave passing the lens undergoes local deformations, much greater than those allowed for by Rayleigh. This is why the eye perceives the image of a point as a radiant spot, rather than a diffraction pattern (1).

But if an eye be stopped at about $d_T = 0.7$ mm, it then begins to perceive quite distinctly and without distortion the diffraction image of a point, which points to that the wave aberrations have approached $^1/_4\ \lambda$.

Now if we place the stop at the periphery of the lens instead of its optical axis, we have to stop the eye down about to $d_T = 0.5$ mm, in order to obtain a diffraction image as clear and undistorted as in the first case.

Fig. 1 shows diagrammatically the wave aberrations of the eye. The horizontal scale and its distortion are given. When the diameter of the eye pupil d_T exceeds the dimensions of the local heterogeneities, the wave aberration h_{max} is great; the image of the point is therefore greatly distorted.

On the other hand, if d_T is smaller than the local heterogeneity (Fig. 1), the wave aberration h^0_{max} counted from the nearest sphere of reference (dotted line) may crop below Rayleigh's allowance, although h_{max} considerably exceeds this magnitude; in this case the eye will observe a perfect diffraction image of the point.

The transition to the nearest sphere of reference is equivalent to a readjustment of the eye, which is achieved at the cost of the accomodation reserve.

This is why, in order to take advantage of the theoretical resolving power of a visual instrument, eye-pieces with an exit pupil $d \cong 0.7$ mm should be applied, while in the case of an eye poorly centered with respect to the eye-piece, the exit pupil should be reduced as much as to $d \cong 0.5$ mm.

Let us call the r e s o l v i n g m a g n i f i c a t i o n a magnification $G_{0.7}$ with d equal to 0.7 mm. It may also be termed maximum magnification, since further increase in magnification scarcely adds any visible details, reducing at the same time apprecіably the surface brightness of the image, and also the contrast sensitivity of the eye.

§ 2. M e a s u r i n g t h e R e s o l v i n g P o w e r o f t h e U n a i d e d E y e. The method of Landolt rings is inadequate, since it estimates r e c o g n i t i o n of the details instead of their r e s o l u t i o n, formula (1) [1] being inapplicable in this case.

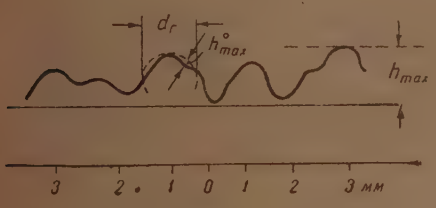

Fig. 1

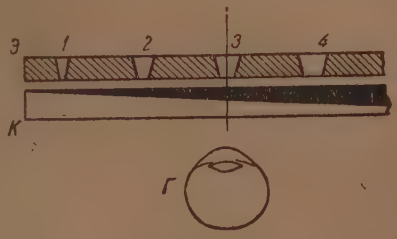

Fig. 2

We have chosen as a test-object an artificial double star with extremely small apertures with considerable separation. The star was illuminated with filtered yellow-green light by means of an illuminating system, the incandescence of the illuminator being controlled by a rheostat. In addition polaroids could be placed both at the artificial double star and at the eye, in order to control the brightness of the star. By varying the distance between the double star and the eye and finding the limit of its resolution, one was able to compute the limit angle of resolution p_Γ.

As l i m i t o f r e s o l u t i o n such an appearance of the double star was adopted, in which the dark bridge between the two nuclei of the images was scarcely perceivable; in this way resolution of the double star and not its recognition was recorded.

In all cases the brightness of the double star was adjusted in order to obtain an optimum brightness at which the limit angle of resolution p_Γ had the minimum value.

In front of the observing eye a screen $\Im$ (Fig. 2) was placed, bearing a large number (up to thirteen) of apertures bored and accurately finished to conical shape; the diameter of the apertures was measured with the aid of a comparator.

Close to the screen a rough photometric wedge K was placed, serving to level out the flows passing through the apertures. This can be done in case the diameters of the equidistant apertures grow in geometrical progression, the constant of the wedge being appropriately chosen. With such a device the eye Γ perceives the double star equally bright, whatever the aperture it is viewed through. Additional adjustment of the brightness ensured optimal resolution. Each time the eye was centered with respect to the axis of the aperture of the screen with the aid of a special procedure.

The experimental curve showing the angle p_Γ as a function of the diameter of the effective aperture of the eye d_Γ is plotted for thirteen points in Fig. 3. It passes through the minimum $p_\Gamma = 128''$ (maximum resolving power of the unaided eye) with d_Γ approximately equal to 1.5 mm. Let us plot the curve p_T for the theoretically resolved angle, limited by diffraction (1). The discrepancy between the two curves may be characterized by the ratio p_Γ / p_T or by the difference $p_\Gamma - p_T$ (Fig. 3).

Let us try to find out: 1) why p_Γ / p_T considerably exceeds unity, and tends toward unity with very small pupils; 2) why $p_\Gamma - p_T$ with small pupils remains at a con-

stant level of about 35″, after which beginning by $d_T \cong 1$ mm, it increases sharply. To do this, let us plot the curves of resolution, which are checked by: 1) diffraction; 2) mosaic structure of the retina; 3) spherical aberration; 4) heterogeneities of the lens (Fig. 4).

The summing up of these curves gives curve p_T obtained experimentally.

The «diffraction» curve has been plotted from formula (1), and raises no doubts. The horizontal straight line of the «mosaic» has been computed assuming the distance between the axes of the cones to be equal to 3 μ, and agrees well with $p_T - p_T$ equal to 35″, which has been found experimentally for small pupils. The curve of «spherical aberration» can be found experimentally: *a priori* its values are very small with small and medium pupils, and it rises steeply along with a further increment of d_T.

The curve of the «heterogeneities» of the lens can be described as the difference between the curve p_T and the sum of the remaining three curves. It assumes an appreciable value with $d_T \cong 1$ mm, and continues growing at first rapidly and then somewhat slower.

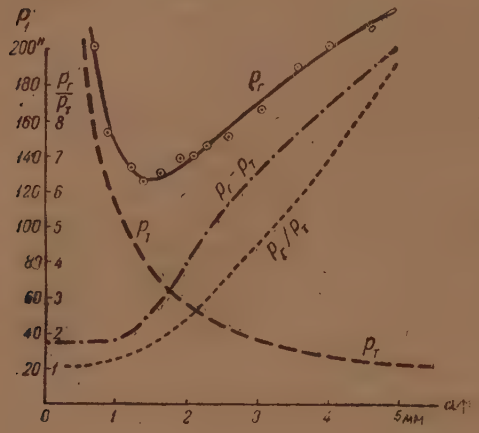

Fig. 3

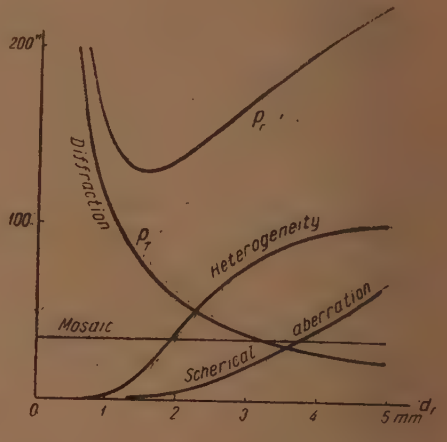

Fig. 4

The writer has shown beyond doubt (2) for his right eye that within nineteen years a considerable change of the shape of the curve p_T took place, and just in the region of the large diameters of the pupil, which may be accounted for solely by that the optical heterogeneities of the lens have perceptibly increased with the age. The physiologists will certainly not fail to give this phenomenon an appropriate interpretation.

§ 3. Resolving Power of the Visual Instruments. If D be the diameter of the objective, and d, the diameter of the exit pupil of the visual instrument, then the magnification is:

$$G_d = \frac{D}{d} \qquad (2)$$

In all the cases where d is less than the eye pupil, the effective aperture of the eye is determined by the value $d_T = d$. If the objective is of first class quality, the eye observing through the instrument will resolve the limit angle P_d, and it is no difficult matter to show that:

$$P_d = \frac{114}{D} \frac{p_T}{p_T} \text{(sec. of arc)} \qquad (3)$$

It is this formula which should be made use of, instead of the poorly founded though generally adopted formula

$$P = \frac{140''}{D} \qquad (4)$$

The table contains the values p_T/p_T for various exit pupils d of the instrument, as well as the values P_d of the limit angle of resolution.

d	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	2.0	2.5	3·	4	5
p_T/p_T	1.00	1.18	1.21	1.25	1.28	1.31	1.42	1.58	2.40	3.34	4.40	6.98	9.80
P_d	$\frac{114''}{D}$	$\frac{135''}{D}$	$\frac{138''}{D}$	$\frac{142''}{D}$	$\frac{146''}{D}$	$\frac{149''}{D}$	$\frac{162''}{D}$	$\frac{180''}{D}$	$\frac{274''}{D}$	$\frac{381''}{D}$	$\frac{502''}{D}$	$\frac{796''}{D}$	$\frac{1120''}{D}$

Formula (4) proved valid for a single special case $d=0.75$ mm only; with $d=5$ mm the resolving power of the visual instrument is 9.8 times less than its theoretical resolving power.

The smaller the optical heterogeneities of the lens, in other words, the younger is the average observer, the more favourable should be the figures of the table, and the larger the exit pupils with which the resolving power of the visual instrument can be turned to profit with all the advantages of the greater brightness of the image of the object.

In this sense a successful observation of the details of planets is the privilege of young observers. The eye most suited for this purpose, however, is the aphakic one, paradoxical as it may seem.

Having proved that the generally adopted formula (4) is inconsistent, for his right eye at least, the author hopes that his results and method will be applied on a sufficiently wide scale in order to determine the properties of the eye of an average observer, this latter being *a sine qua non* condition for an adequate designing and computing of visual optical instruments.

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PHYSICAL CHEMISTRY

ON TYPES OF KINETIC CURVES IN CHAIN REACTIONS

I. LAWS OF THE AUTOCATALYTIC TYPE

By N. N. SEMENOV, Member of the Academy

The object of this paper is to prove in greater detail a statement made by me in an earlier paper (1). Namely, that for the simplest cases of chain reactions the equations of chain kinetics coincide practically with the ordinary equations of autocatalysis by ultimate products. This correspondence is purely formal, since the ultimate products of the chain reactions do not usually have any accelerating influence on the chemical process. Still the fact is important from the practical point of view, for it opens a possibility of simplifying considerably every kind of kinetic calculation connected with the velocity of chain reactions.

When the pressure of the initial substance is much above the lower limit, the equation of chain kinetics may be written as a system of two differential equations

$$\frac{dn}{dt} = n_0 + an; \qquad -\frac{dU}{dt} = n_0 + en \tag{1}$$

where n [U] is the number of molecules of the active half-product [initial substance] in a unit volume at a given instant t; an is the velocity of the reaction of chain branching; en, the velocity of transformation of the initial substance in the chain developing reactions.

According to the reaction, the quantity e may be equal to or larger than a; so that $e/a = q \geqslant 1$*; n_0 is the velocity of the primary reaction of the initial substances of the generating molecule of the active half-product, which serve as centres of the initiation of chains.

It has been proved by me (2) that by such two equations the kinetics of a complicated chain reaction proceeding with the aid of several varieties of active half-products can be described as well. By n should then be meant the concentration of that active half-product which is the slowest in undergoing conversion. The quantities a and e may be complicated functions of the amount U of the initial substance.

Let us consider the simplest case where

$$a = f\frac{U}{U_0}; \qquad e = c\frac{U}{U_0}; \qquad n_0 = n_0'\frac{U}{U_0}$$

U_0 being the original concentration of the initial substance.

Adopting the notation $\frac{U}{U_0} = 1 - \eta$; $\frac{U_0 - U}{U_0} = \eta$; $\frac{n}{U_0} = \xi$; $\frac{n_0'}{fU_0} = \nu_0$; $\tau = ft$

* In the rare cases of strongly branching chains q may be smaller than one, and take the value of 0.5, for instance.

and $q=\frac{e}{a}=\frac{c}{f}$, re-write the system (1) in the form

$$\frac{d\xi}{d\tau}=(\nu_0+\xi)(1-\eta); \qquad \frac{d\eta}{d\tau}=(\nu_0+q\xi)(1-\eta) \tag{2}$$

Here $\xi=\eta=0$ for $\tau=0$ and $\eta=1$ for $\tau=\infty$.

The equation for autocatalysis by final products will run thus

$$\frac{d\eta}{dt}=k\eta(1-\eta)$$

or, because the course of the reaction must necessarily involve, along with autocatalysis, the formation of the ultimate product through a direct reaction of the initial substance [whose velocity we put at $kN_0(1-\eta)$]

$$\frac{d\eta}{dt}=k(N_0+\eta)(1-\eta)$$

or again, putting $\tau=kt$

$$\frac{d\eta}{d\tau}=(N_0+\eta)(1-\eta) \tag{3}$$

Integration of (3) gives

$$\eta=\frac{N_0[e^{(1+N_0)\tau}-1]}{1+N_0e^{(1+N_0)\tau}} \tag{4}$$

or

$$\tau=\frac{2.3}{1+N_0}\log\frac{(1+\eta/N_0)}{1-\eta} \tag{5}$$

For $N_0 \ll 1$ we have, accordingly,

$$\eta=\frac{N_0(e^{\tau}-1)}{1+N_0e^{\tau}} \tag{4'}$$

and

$$\tau=2.3\log\frac{1+\eta/N_0}{1-\eta} \tag{5'}$$

Now we proceed to an approximate integration of system (2), confining ourselves for the time being to the case of small ν_0, which is much the most interesting. Put $\nu_0 \ll \xi_1$ where $\xi_1=0.01/q$.

Then the term ν_0 of equation (2) may be neglected in the region $\xi>\xi_1$, and the system (2) will read then as follows

$$\frac{d\xi}{d\tau}=\xi(1-\eta); \qquad \frac{d\eta}{d\tau}=q\xi(1-\eta) \tag{6}$$

Examining the equations (2) and (6), we can readily see that if ν_0 is small and $\eta>0.01$, then $\eta\simeq q\xi$.

Thereby the system (6) is reduced to a simple equation

$$\frac{d\eta}{dt}=\eta(1-\eta) \tag{6'}$$

which is a usual autocatalytic equation. Equation (6') holds for $\eta>\eta_1=0.01$. By integrating we get

$$\eta=\frac{\eta_1e^{\tau-\tau_1}}{1+\eta_1e^{\tau-\tau_1}} \tag{7}$$

This solution, however, affords no possibility of constructing η as a function of τ from the start of the reaction ($\tau=0$), since selecting arbitrarily some $\eta=\eta_1$, say $\eta_1=0.01$, we do not know what is the time τ_1 that corresponds to it. In order to solve this problem, one should pay attention to the fact that for $\eta\leqslant 0.01$ we may put $1-\eta\cong 1$ in the fundamental equations (2) and then integrate the system (2), to obtain

$$\xi=\nu_0(e^{\tau_1}-1) \tag{8}$$

and

$$0.01 = \eta_1 = q\nu_0[e^{\tau_1} - 1 - (1 - 1/q)\,\tau_1] \tag{9}$$

under the condition that $\nu_0 \ll 0.01/q$ or $\eta_1/q\nu_0 \gg 1$.

It is also obvious that $e^{\tau_1} \gg 1 + (1 - 1/q)\,\tau_1$ and, therefore, with sufficient approximation $\xi = \nu_0 e^{\tau_1}$ and $\eta_1 = 0.01 = q\nu_0 e^{\tau_1}$. Substituting in (7) the obtained value of η_1 we get

$$\eta = \frac{q\nu_0 e^{\tau}}{1 + q\nu_0 e^{\tau}} \tag{10}$$

As for $\tau > \tau_1$ we have $e^{\tau} \gg 1$, the solution (10) is equivalent to the solution (4′) of the autocatalytic equation

$$\frac{d\eta}{d\tau} = (q\nu_0 + \eta)\,(1 - \eta) \tag{11}$$

or

$$\tau = 2.3 \log \frac{1 + \eta/q\nu_0}{1 - \eta} \tag{12}$$

and this is what was to be demonstrated.

In the particular case where $q = 5$ and $\nu_0 = 0.000033$, the condition $\nu_0 = 0.000033 \ll 0.01/5 = 0.002$ is fulfilled. Then $\eta_1 = 0.01 = 5\nu_0\,(e^{\tau_1} - 1 - 0.8\tau_1)$ gives $e^{\tau_1} - 1 - 0.8\tau_1 = 60$ or $\tau_1 = 4.17$ and $e^{\tau_1} = 60$, which is much larger than $1 + 0.8\tau_1 = 4.3$.

The corresponding autocatalytic equation is

$$d\eta/d\tau = (5\nu_0 + \eta)\,(1 - \eta) = (1.65 \cdot 10^{-4} + \eta)\,(1 - \eta)$$

and

$$\tau = 2.3 \lg \frac{1 + \eta/5\nu_0}{1 - \eta} = 2.3 \log \frac{1 + 6000\,\eta}{1 - \eta}$$

To this case refers the curve in Fig. 4 bringing out the variation of η as a function of τ.

Yet for large ν_0, too, the system of chain reactions (2) can be approximately described by a suitably chosen autocatalytic equation with the constants f and q somewhat modified as against (11).

Dividing the first of the equations (2) by the second, we get $\frac{d\xi}{d\eta} = \frac{\nu_0 + \xi}{\nu_0 + q\xi}$

Table 1

ξ/ν_0	λ	$0.8\,\lambda$	η/ν_0	ξ/ν_0	λ	$0.8\,\lambda$	η/ν_0
0.1	0.95	0.76	0.12	10	0.24	0.19	40.5
0.2	0.91	0.73	0.27	20	0.153	0.12	88
0.4	0.84	0.67	0.66	40	0.093	0.074	186
0.6	0.78	0.62	1.14	60	0.068	0.054	285
0.8	0.73	0.58	1.67	80	0.055	0.044	375
1.0	0.69	0.55	2.25	100	0.046	0.037	480
1.3	0.64	0.51	2.95	200	0.026	0.021	980
1.5	0.61	0.44	3.42	300	0.018	0.014	1490
2	0.55	0.44	5.6	500	0.012	0.0095	~ 2500
4	0.405	0.32	13.6	800	0.008	0.0064	~ 4000
6	0.325	0.26	22	1000	0.007	0.0056	~ 5000
8	0.275	0.22	31				

and, since $\eta = 0$ for $\xi = 0$, we can write

$$\frac{\eta}{\nu_0} = q\frac{\xi}{\nu_0}\left[1-\left(1-\frac{1}{q}\right)\frac{\nu_0}{\xi}\ln\left(1+\frac{\xi}{\nu_0}\right)\right] = q\frac{\xi}{\nu_0}\left[1-\left(1-\frac{1}{q}\right)\lambda\right] \quad (13)$$

where

$$\lambda = \frac{\nu_0}{\xi}\ln\left(1+\frac{\xi}{\nu_0}\right).$$

Let us consider a special case: $q = 5$ and

$$\frac{\eta}{\nu_0} = 5\frac{\xi}{\nu_0}[1-0.8\lambda] \quad (14)$$

We set out the variation of η/ν_0 with ξ/ν_0 in tabular form (Table 1).

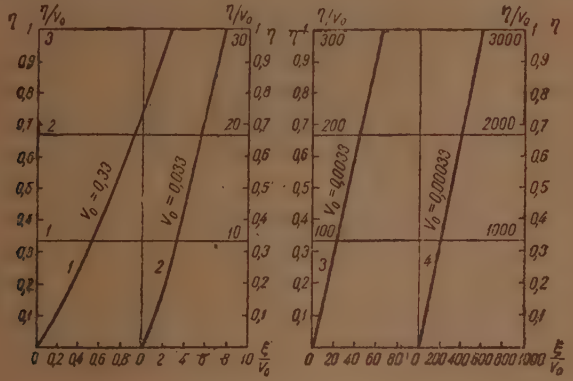

Fig. 1

In Fig. 1 the data of the table are represented graphically. The curves *1*, *2*, *3* and *4* bring out η/ν_0 in the intervals ξ/ν_0 ranging from 0 to 1.5, from 0 to 10, from 0 to 100 and from 0 to 1000, respectively. Every next curve is drawn on a scale that is 10 times as small as the scale of the preceding curve. On the axes the values of $\eta = \frac{\eta}{\nu_0}\nu_0$ are also marked off: for 1) $\nu_0 = 0.33$, 2) $\nu_0 = 0.033$, 3) $\nu_0 = 0.0033$ and 4) $\nu_0 = 0.00033$.

Knowing the curves of Fig. 1, we can compute the dependence of η on ξ for any particular value of ν_0 and find $\xi = \psi(\eta)$.

As $5\xi = 5\psi(\eta)$, the equation $d\eta/d\tau = (\nu_0 + q\xi)(1-\eta)$ reduces to $d\eta/d\tau = [\nu_0 + \psi(\eta)](1-\eta)$.

For $\nu_0 = 0.00033$ (Fig. 1, curve *4*) the variation of η/ν_0 with ξ/ν_0 is practically a straight line: $\eta = 5\xi$, and so in this case the chain equations are reduced to the autocatalytic equation mentioned above. However, it may be seen from curves *1* and *2* that even with considerably smaller ξ/ν_0 and η/ν_0, that is considerably greater ν_0, the relation between these quantities on an interval of notable extension is very nearly a linear one, but the slope is less than 5. Thus, in the interval $\frac{\eta}{\nu_0} - \frac{\xi}{\nu_0}$; 0—1.5 (curve *1*) we see that for $\eta/\nu_0 > 0.6$ or (if $\nu_0 = 0.33$) for $\eta > 0.2$ this relation is expressed very well by the straight line $\frac{\eta}{\nu_0} = 3\left(\frac{\xi}{\nu_0} - R\right)$, where $R = 0.2$ or $\eta = 3(\xi - 0.2\nu_0)$. Hence $5\xi = 1.65\eta + \nu_0$ or

$$d\eta/d\tau = (5\xi + \nu_0)(1-\eta) = (2\nu_0 + 1.65\eta)(1-\eta) \quad (15)$$

In order to lessen the divergence for $\eta < 0.2$, one has to reduce R, or,

in other words, to shift the straight line somewhat to the left. Put

$$d\eta/d\tau = (1.65\nu_0 + 1.65\eta)(1-\eta)$$

or

$$d\eta/d\tau = 1.65(\nu_0 + \eta)(1-\eta) \qquad (16)$$

This autocatalytic equation gives upon integration according to (5 for $\nu_0 = 0.33$

$$\tau_a = \frac{2.3}{(1+\nu_0)\,1.65} \log \frac{1+\eta/\nu_0}{1-\eta} = 1.05 \log \frac{1+3\eta}{1-\eta} \qquad (17)$$

To compare with true values, let us compute η as a function of τ from the exact equations (2).

For this purpose we may use the plot 1 to draw up a table of values of η and $d\eta/d\tau = (\nu_0 + 5\xi)(1-\eta)$ for different values of ξ (columns 1 and 2, 3 and 4, 5 and 6 of Table 2); $\nu_0 = 0.33$.

Table 2

ξ/ν_0	$5\,\xi/\nu_0$	5ξ	η/ν_0	η	$d\eta/d\tau = (\nu_0+5\xi)(1-\eta)$	τ	τ_a
1	2	3	4	5	6	7	8
0	0	0	0	0	0.33	0	0
0.1	0.50	0.165	0.12	0.04	0.48	0.1	0.07
0.2	1	0.33	0.27	0.09	0.6	0.19	0.16
0.4	2	0.66	0.64	0.21	0.79	0.36	0.33
0.6	3	1	1.13	0.37	0.84	0.56	0.55
0.8	4	1.32	1.68	0.55	0.74	0.79	0.8
1	5	1.65	2.25	0.74	0.52	1.09	1.14
1.1	5.5	1.8	2.55	0.84	0.34	1.32	1.4
1.2	6	2.0	2.8	0.93	0.16	1.68	1.8

For $\eta = 0.04$ we compute τ from the exact formula (9), to obtain $\tau_{0.04} = 0.098$. Then we compute

$$\Delta\tau = \frac{\eta_2 - \eta_1}{1/2\,[(d\eta/dt)_2 + (d\eta/dt)_1]} = \frac{0.05}{0.54} = 0.093$$

$$\tau_2 = \tau_{0.04} + \Delta\tau_1 = 0.098 + 0.093 = 0.19$$

Then $\Delta\tau_2$, $\Delta\tau_3$ and so on are calculated in the same way.

Thus, we obtain the 7th column in which are the values of τ corresponding to different values of η, in accordance with the system of equations (2) for $q = 5$ and $\nu_0 = 0.33$.

The values of τ_a in column 8 have been calculated by means of the autocatalytic formula (17). They are seen to be in a fairly good agreement with the values obtained for τ, which testifies to the applicability of the autocatalytic formula in the case of chain reactions with large ν_0.

In Fig. 2 the continuous curve brings out the kinetics of the chain reaction for $q = 5$ and $\nu_0 = 0.33$, according to the exact solution (column 7), and the dotted curve is plotted on the values computed according to the autocatalytic formula (17) (column 8).

For $\nu_0 = 0.033$ a similar table can be composed on the basis of the curve 2 (Fig. 1). Noting that in this case the slope of the straight line $\eta - \xi$ is close to four, we form the autocatalytic equation

$$d\eta/d\tau = 1.27(\eta + 2\nu_0)(1-\eta) = 1.27(0.066+\eta)(1-\eta) \qquad (18)$$

from which we have

$$\tau_a = 1.68 \log \frac{1+15\eta}{1-\eta} \qquad (19)$$

The true values of τ are calculated as in the previous case. The data thus secured are given in Table 3.

Table 3

5ξ	η	$\frac{d\eta}{d\tau}$	τ	τ_a
2.5	0.03	0.114	0.4	0.3
5	0.076	0.188	0.75	0.6
10	0.15	0.31	1.05	0.98
15	0.32	0.36	1.55	1.56
20	0.44	0.39	1.87	1.9
25	0.59	0.355	2.28	2.3
30	0.73	0.28	2.72	2.76
35	0.9	0.19	3.44	3.65

It will be obvious that here, too, the accurate data are not badly reproduced by the autocatalytic formula. The data of Table 3 are represented gra-

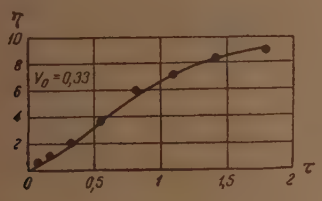

Fig. 2.

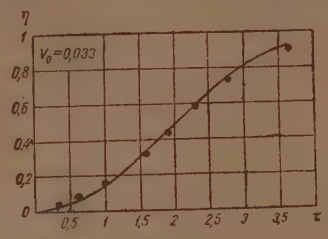

Fig. 3.

phically in Fig. 3, where the dots give values calculated according to the autocatalytic formula (19). Thus, if one comes in an experiment across a curve of the autocatalytic type $d\eta/dt = (\nu_0 + \eta)(1 - \eta)$, and has once estab-

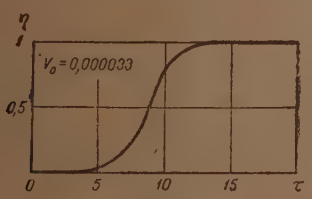

Fig. 4.

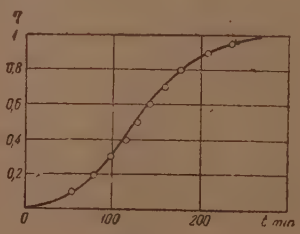

Fig. 5.

shed that the final product does not accelerate the reaction, there is every reason to believe that this is a chain reaction with branching chains.

Many experimental curves rather closely follow the above-mentioned autocatalytic laws of the type $t = A \ln \frac{1 + B\eta}{1 - \eta}$, where A and B are certain constants.

As examples of S-shaped symmetrical curves of the type represented in Fig. 4, one may mention the decomposition of mercaptane according to Tyler [1], the oxidation of pentane according to Eggerton [1], the oxidation of hydrogen under low pressure [1] and many other instances. The type of curve shown in Fig. 3 is exemplified by a typical curve of the decomposition of Cl_2O [3] (Fig. 5).

In Fig. 5 the theoretical curve $t_{\min} = 37.7 \ln \frac{1 + 30\alpha}{1 - \alpha}$ is represented as a continuous line. The dots indicate the experimental data of the above authors

(for $T = 100°$ C, $p = 412.8$). To put examples for the type of curve given in Fig. 2, I can refer to the oxidation of methanol, according to Fort and Hinshelwood (4); of ethylene, according to Thompson and Hinshelwood (5); of acetylene, according to Spence and Kistjakowsky (6); of formaldehyde, according to Fort and Hinshelwood (4) and several others.

Here I give, by way of example, the theoretical curve $t_{\min} = 3.8 \ln \frac{1+5x}{1-\alpha}$ and the experimental values (dots) for the oxidation of CH_3OH, according to Fort and Hinshelwood (4) (Fig. 6). It is interesting to note that when active substances of the type NO_2, $HCHO_x$, *etc.*, are added to a mixture of a hydrocarbon with oxygen, the kinetic curves undergo a sharp change and pass from the type of Fig. 4 to that of Fig. 2.

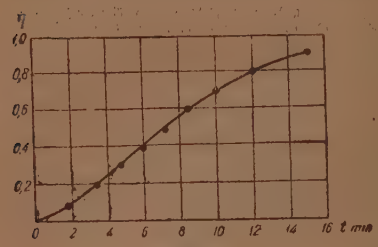

Fig. 6

This is because these substances, while reacting with the initial substance, generate great number of initial active centres, which are few when the reaction proceeds between pure substances. It is thus that ν_0 rises from very low values to high.

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BIOCHEMISTRY

ON THE NATURE OF GLOBULAR PROTEINS

II. A FEW CONSEQUENCES OF THE NEW HYPOTHESIS

By S. E. BRESLER and D. L. TALMUD, Corresponding Member of the Academy

1. If the number of hydrophobic chains is very small or the number of sharply expressed hydrophilic side-chains is very large, the polypeptide chains will not be folded into a globula. This is illustrated by the fibrillar proteins, on the one hand, and protamine and gelatine, on the other. The fibrillar proteins like fibroin silk are built up from aminoacid residues of a few different kinds, the side-chains being here either completely absent (glycine 43.8 per cent) or very short (alanine 26.4 per cent). The fibrillar proteins like keratines, which are built up from aminoacid residues of several kinds, still contain a 2—3 times smaller number of pure hydrocarbon side-chains than globular proteins. Keratines contain, besides, the largest quantity of tetrafunctional cystine compared with any known protein. The presence of cystine leads to a space polycondensation of the protein. The folding and unfolding of molecular chains of keratine is therefore possible in a limited range only, since the chains are chemically linked with each other by sulphur bridges.

The strong prevalence of hydrophilic side-chains in protamines (in salmine 87.4 per cent of arginine, 7.8 of serine) and in gelatine (14.1 of oxyproline, 25.5 of glycine) in the case of a small number of hydrocarbon side-chains does not entail the formation of globulae. The sedimentation diagram of gelatine has therefore a sharply expressed polydisperse character.

The absence of the conditions for the formation of globulae in protamine and in gelatine, and to a certain extent in caseine and alcohol soluble proteins is equivalent to the absence of the mechanism taking care of the selection of relatively monodisperse polypeptide chains.

2. The first step towards the synthesis of globular proteins are perhaps the interesting experiments of Frankel and Katchalski [1]. In the process of polycondensation of ethyl esther in non-aqueous solutions they have obtained polyaniline which is soluble in water (in contradistinction from the non-soluble polyglycine). The degree of polymerization of polyalanine ($n = 23$) with respect to the order of magnitude agrees satisfactorily with the calculated size of minimum globula, which consist of a polypeptide chain with methyl side-chains only.

3. The phenomenon of the intramicellar solubility, studied in detail by Mac-Bain [2] on solutions of detergents and denoted by him as «solubilization», is also observed in solutions of globular proteins [3].

This points to a fundamental analogy between the structure of a soap micelle and the structure of the protein globula. To the hydrophobic «nucleus» which is wholly covered by the hydrophilic polypeptide «envelope», there corresponds in the case of a soap micelle a double hydrophobic layer surrounded by polar groups.

4. The minimum condition of the energy of the protein globula coincides with the conditions of its largest solubility. This does not mean, however, that other states of the protein particle with a decreased solubility are impossible.

The unfolded polypeptide chain, containing hydrophobic side-chains, possess in an aqueous medium a much larger energy than when folded into a globula. In the unfolded state, however, the entropy of the macromolecule is also strongly increased, owing to the enormous rise of the number of statistically possible configurations. The simultaneous increase of the energy, *i. e.* of the factor decreasing the statistical probability of a given state, and the increase of the entropy, *i. e.* of the factor increasing its probability, mutually compensate each other. A new state thus makes its appearance, which is stable in spite of the unfoldening of the globula. This is the denaturation which arises simply as a result of an increase of temperature.

From the above argument it becomes clear that the difference of the free energies $\Delta\Phi = \Delta U - T\Delta S$ of the folded and unfolded states of a polypeptide chain can be very small, while the energy difference ΔU and, consequently, the entropy difference ΔS is very large ([4]).

In the case of transition from the globular state to the unfolded, *i. e.* to the denaturated one, the free energy passes through a maximum which corresponds to an intermediate state of folding, when the increase of entropy compensates in the poorest way the rise of energy.

From the sharpness of this maximum there follows an enormous magnitude of the temperature coefficient of the denaturation reaction $\left(\frac{kT + 10^\circ}{kT} = 600\right)$ which is quite unusual for the chemical kinetics of macromolecules, but perfectly natural in this case.

Along with the enormous rise of the energy of an unfolded denaturated state, the solubility of the protein in the isoelectrical state falls off extremely sharp, owing to the appearance of a large boundary surface of the hydrophobic side-chains with water. By charging the hydrophilic groups of protein with ions this insolubility can be compensated.

5. Pauling's hypothesis ([5]) on the structure and process of formation of antibodies, recently crowned by an artificial preparation of antibodies ([6]), does not imply a definite mechanism of folding and unfolding of the globulae. Making use of our considerations, it is, however, easier to assume that in a molecule of γ-globulin, *i. e.* in an associate of 8 minimum globulae, the end globulae are less stable than the inner ones and can assume configurations which are complementary to certain portions of the surface of the antigen.

This is also supported by the decomposition of the molecules of serum pseudoglobulin into monodisperse particles of $^1/_2$ and $^1/_4$ of the initial value in the case of proteolysis ([7]), whereas, according to Pauling, one is compelled to assume that a polypeptide chain possesses a different stability in its various parts.

6. In conclusion it is necessary to note that small periods of identity observed by Bernal ([8]) on X-ray diagrams of moist crystals of globular proteins, which point to the existence of a certain order in the architecture of the crystals up to interatomic distances, do not contradict the relative character of the monodispersity of globular particles. The X-ray pattern regularity refers most probably to an orderly packing of the folded polypeptide chain, while the distribution of the side-chains in a «nucleus» can be but approximately regular, since the side-chains of diverse aminoacid residues differ too much from each other with respect to their size.

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MINERALOGY

THE AUGITES FROM TALYSH (AZERBAIDJAN)

By Mir-Ali KASHKAI

(Communicated by D. S. Beliankin, Member of the Academy, 3. XI. 1943)

Within the boundaries of Mountainous Talysh in the upper course of the Kyandji-byaru river, upstream of the villages of Pirazora and Goveri, up to the Kosmolyan and Ghilider villages, and in a latitudinal direction from the Mistan village to the Dighya village, there are exposures of black augite tuffs. As to its lithological composition this series is sharply distinguished from the overlying basalt and tuff cover referring to the Middle Eocene (Lutetian stage). The black augite tuffs are overlain by a thick (over 100 m) series of grey tuff-sandstones in which the fauna found by the author (between the villages of Pirazora and Dighya), according to the determination of V. V. Bogachev, is represented by *Nummulites atacicus* Leym—a species characteristic of the Lutetian stage. Thus, their age is established as pre-Middle Eocene. The exposure of this tuff of deeper lying horizons in the upper course of the Kyandji-byaru is produced by a fault along the more persistent cover of analcime andesite-basalt (²).

The cementing mass of black augite tuff is subject to granular disintegration, owing to which the rock becomes loose, magnetite and particularly well-developed crystals of augite being easily separated from it. Between the villages of Pirazora and Dighya the author collected over 1000 crystals of augite. These crystals are further carried away to the Caspian Sea and then cast ashore by the waves, forming the so-called magnetite-augite sands of the Lenkoran-Astara coast.

In fissures, voids and veins of the rock described there occurs calcite which in some places is burnt by the population for lime production.

The groundmass of the augite tuff is mainly vitrophyric texture. In phenocrystals, in addition to large prisms of monoclinic pyroxene, there is observed also a plagioclase of the Labrador series and an ore-mineral, secondary chlorite-serpentine, especially in small voids in the rock.

The relatively infrequent occurrence of abundant material on augites induced the author to a detailed study of the Talysh minerals. The size of the crystals is from 1 to 2 mm (up to 1 cm along the long axis). The colour is dark-green to black.

With regard to habit, two types of augite are distinguished among them: the short-prismatic and the long-prismatic type. It is of interest to note that either of these types taken separately is confined to a definite massif. For example, in the upper course of the Kyandji-byaru river, on the left slope at the Pirazora village, the augite crystals were found to be exclusively short-prismatic, while some kilometers further north-westward in the outcrop downstream of the Dighya village they were long-prismatic.

Type I, Short-prismatic. The crystals are considerably shortened in a vertical direction. A measurement of the crystals on the goniometer

enabled the following forms to be established: *a* (100), *m* (110), *b* (010), *s* ($\bar{1}11$), *z* (021), Θ ($\bar{2}21$), *p* ($1\bar{0}1$).

The best developed are *m* (110) and *s* (111). Of the pinacoids *b* (010) is considerably wider than *a* (100) but much shortened. The remaining forms: *p* (101), *z* (021) and Θ ($\bar{2}21$) occur as slight traces or, more frequently, are altoge ther lacking. Twins along *a* (100) are encountered much rarer than single crystals.

Type II, Long-prismatic. The crystals are markedly elongated along the vertical axis. The forms observed are the same as in the first type but are distinguished by that the faces of the pinacoid *a* (100) are wider than those of *b* (010), which are not infrequently developed as a narrow band. A characteristic distinctive feature is presented also by the strong development of the negative pinacoid *p* ($1\bar{0}1$) which is nearly always present and in some cases is developed to a considerable extent. Twins along *a* (100) are rather common and are observed more frequently than in the first type.

As regards refringence and specific gravity the two types of augite are not sharply different. Still, both constants are somewhat higher in the case of the long-prismatic type.

Type and deposit	N_g	N_p	Sp. gravity
Short-prismatic augite at the Pirazora village .	1.711	1.692	3.4625
Long-prismatic augite at the Dighya village . .	1.716	1.692	3.5347

The microstructure and the other optic characteristics are similar. Inclusions of glass and magnetite are frequent. Of the greater part of the crystals a twin structure and a zonal are characteristic. The angle of extinction, CN_g, in the central portions of the zonal crystals is 43—44°, and on the periphery, 40—41°; $+2V = 56—58$.

Chemically, the two types of augites described, having a different habit of crystals, are also similar, an evidence of which is presented by the analyses (Nos. 1 and 2) cited below (see table).

Oxides	1		2		3
	Weight per cent	Molec. quant.	Weight per cent	Molec. quant.	Weight per cent
SiO_2	47.01	0.785	47.42	0.773	47.79
TiO_2	0.86	—	0.68	—	—
Al_2O_3	3.22	0.031	4.34	0.042	13.18
Fe_2O_3	7.83	0.049	6.04	0.038	4.84
FeO	5.03	0.074	4.57	0.064	4.77
CaO	22.14	0.394	21.44	0.382	21.81
MgO	13.10	0.327	14.50	0.362	8.34
R_2O	0.24	0.003	0.17	0.003	—
H_2O_{-110}	—	—	—	—	—
H_2O_{+110}	0.74	—	0.91	—	0.48
Total . . .	100.17	—	100.07	—	100.16

No. 1, augite from the exposure at the Pirazora village; type I, short-prismatic.
No. 2, augite from the exposure downstream of the Dighya village; type II, long-prismatic.
No. 3, augite from the andesite from the Imeretinskaya Mt. (4).

Recalculating analyses 1 and 2 to molecular quantities and then to the composition of the augites, the following is obtained (for both):

$$CaO\,(Mg,\ Fe'')\,O \cdot 2SiO_2 \cdot 0.2\,(Al,\ Fe''')_2\,O_3$$

Of the Caucasian augites, described in the literature, an outward resemblance to the Talysh augites is shown by the pyroxene crystals from the locality «bet-

ween the Suram pass and the Zvarsky gorge», described by S. F. Glinka. Unfortunately, their analyses are not given.

The crystals of pyroxene from the andesite and basalt rocks of the Imeretinskaya Gora (Mt.) and the Kokhta spur in the vicinity of the town of Bakuriani analysed by N. N. Smirnov, differ from those described by the author both with respect to the magma to which they belong and to their chemical properties (see table, column 3).

Considering that the crystallization of the two types of augite occurred from the magnetic melt, the difference of forms may be caused by: (1) the presence of admixtures or catalysts and a certain change in the composition of the magma; (2) a change of temperature in different portions of the magma near the enclosing rocks; (3) the direction of movement of the magma, and (4) the direction of the forces of compression at the moment of crystallization of the minerals.

In viewing the crystals investigated from this standpoint, it may be assumed that the short-prismatic crystals with an ideal and even development of faces and a comparatively lesser (with regard to percentage) twin structure were freely floating in the magma, while the long-prismatic crystals characterized also by a frequent twin structure and intergrowths, were influenced by the forces of compression or the mobile state of the magma.

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PLANT PHYSIOLOGY

AGE VARIATIONS IN THE ABSORBING ACTIVITY OF ROOT SYSTEMS

By O. S. SEMENOVA

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A variety of problems arise in agriculture when one has to decide upon how to till the land, at what time and how deep to manure it, to what depth should moisture be conveyed on irrigation and so on. For their successful solution these problems depend upon what we know about the variations that take place with increasing age in the absorbing activity of root systems. Up to the present our knowledge in this matter has been very scarce. To acquire the necessary information it is essential, in my opinion, to start by studying from that angle the relation between the absorption of mineral elements and water.

This relation has more than once invited the attention of investigators, but no single conclusion has been reached until now. Some of the workers in this field ([3], [11]) have reported the existence of a direct dependence between the absorption of water and the absorption of mineral food by the plant. Others, on the contrary, believe that the roots absorb mineral elements independently of water ([1], [5], [10]). Finally, there has been expressed the opinion ([2]) that with increased absorption of water only some of the mineral elements are liable to be absorbed at a higher rate. One of the reasons that may be put forward to account for the difference of opinion on the subject, is that no account has been taken of the age variations which may affect the ratio of the absorbed water to the uptake of nutrient elements dissolved in it. In fact, age variations have certain influence on the absorption of food according to some literary data. Thus, Ovechkin and Burian ([6]) have studied the absorption of matter by the whole plant and found that at early phases of development the amount of mineral elements absorbed by the plant is by far greater than their content in the volume of absorbed water. Ovechkin and Burian have used the ratio:

$$\frac{\text{amount of absorbed nutrients}}{\text{amount of nutrients in the volume of absorbed water}} \cdot 100$$

to describe what they called the intensity of absorption. In terms of this ratio, the absorption of potassium by the millet in the phase of tillering amounts, according to these authors, to 699 per cent; the absorption of phosphorus to 1500 per cent. As the development of the plant goes on, the intensity of absorption goes down, to become 100 per cent for potassium, 13 per cent for phosphorus, at the time of wax ripeness. But the data obtained by Ovechkin and Burian give no answer to the question we are interested in. We still remain unaware of the complexity of the changes which the absorbing activity of the root system is liable to suffer in a developing plant.

First of all, it is well to point out that even if the absorbing activity of the living roots is entirely eliminated, the plant may still take up water through its dead roots ([4]). It does so owing to the sucking power of its transpiring leaves.

Thus, a purely passive absorption of water by part of the roots enters the picture. According to Renner (7), the passive absorption accounts for a major portion of the water flow travelling through the living root system. Along with it, an active absorption of water is constantly in operation, as the experiments by Sabinin(8) have shown. The relation between the processes of active and passive absorption will not, of course, remain constant throughout the development of the plant. It rather changes as the root system gains in age, depends also upon the transpiring leaf area and finally varies with the conditions under which the plant makes its development.

Secondly, the amount of absorbed matter was referred by Ovechkin and Burian to the whole root system. Yet the size of the root system is liable to continuous variation in the course of development. So it cannot possibly be used as a standard unit of reference. It is a far better practice to do what Sabinin and Kolosov did (8) and refer the absorbed quantities to a unit surface or unit volume of the living root.

Accordingly, the task I had set myself in the present work was to separate the active absorption of water from the passive absorption and in doing so to trace the age variations in the active absorption of water and of nutrient matter dissolved in it, referring the detected amounts to the unit volume of the living root.

Method and Results. The experiment was run in the greenhouse of the Timiriazev Institute of Plant Physiology, Academy of Sciences of the USSR. For test-object were used the plants of *Vicia Faba*, grown in water on Knop's solution. 3 days before starting the experiment they were placed in a tap water acidulated to pH = 6.3. After that their root system was carefully washed with tap water and distilled water. The roots were then put into volumeters of the type described by Sabinin and Kolosov. These devices served to measure the daily absorption of water and mineral food: K, Ca and P, by the plant. The volumeters with the plants were transferred to a glass chamber, 1.5 m long, 0.75 m wide and 1 m high.

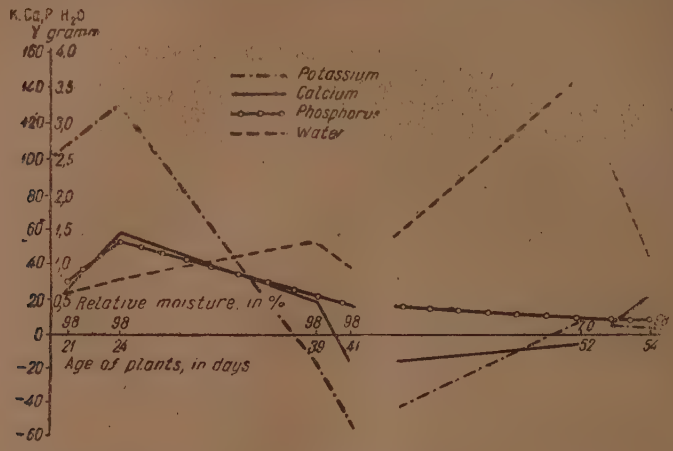
For some of the test-plants in this chamber the relative humidity of air was increased in order to suppress transpiration and thereby decrease the passive absorption of water. This was achieved by means of pans with water, placed at the bottom of the chamber. The relative humidity of the air was measured by the psychrometer of August. Its fluctuations did not go beyond 1—2 per cent. The absorption of water was estimated by adding distilled water from a dropper until the meniscus was brought back to its initial position in the volumeter tube. The accuracy of this estimation was up to 0.05 cm^3. The absorption of mineral nutrients was determined from the change in the concentration of solution outside the plant. Potassium was estimated by the cobalt-nitrite method; calcium, according to Clarke; phosphorus, according to Fiske and Subbarow. The volume of living roots was determined by the method described in the above paper by Sabinin and Kolosov. The experiment was run in five replicates and all of them showed the same trend of the absorption process for every element tested.

In the adjoined figure the results are represented graphically on the basis of the average data. Six tests were made on every plant at different periods of its development. The age of the plants is plotted along the axis of abscissae, while the ordinates indicate the amounts of absorbed mineral elements—K, Ca, P—in γ and of water in grams.

The curves show plainly that the amount of mineral food and water being absorbed by the roots is liable to change with increasing age. Its maximum rate of absorption, that is the amount of substance absorbed in 24 hours by a unit volume of root, was attained when the plants were 24 days old, bearing 6 or 7 leaves and starting to send forth lateral shoots. From then on the absorption of mineral food decreased steadily. While 53 γ of phosphorus was absorbed at the age of 24 days, 17 γ was absorbed at the age of 39 days, and only 7 γ at the age of 52 days. In the case of calcium the curve of absorption goes down more abruptly still: 24-day-old plants were taking up 57 γ of calcium, but at the age of 41 days

the same plants were even giving back some of their calcium to the nutrient medium. In the case of potassium the decrease is expressed with especial sharpness.

Contrary to this, the rate of absorption of water is nearly invariable when the relative humidity of the air is high. Of course, the plant takes up increasing amounts of water as it increases in age, but parallel grows its root system, and so, until a certain point in development is reached, the rate of water absorption, as referred to unit volume of root, changes very little. When at the age of 52 days the relative humidity of the air was reduced for some of the plants to 70 per cent



of what it has been before, these plants increased three times the rate of water absorption compared to the other plants. This increase in the absorption of water under conditions of enhanced transpiration set up by the reduction of air humidity, was probably brought about by way of passive absorption. But at the same time there was no parallel increase in the absorption of mineral food. This may be interpreted to mean that the absorption of mineral nutrients by the root system is largely an active process.

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PHYSIOLOGY

AN ANALYSIS OF THE MODE OF ACTION OF ACETHYLCHOLINE AS CHEMICAL AGENT OF NERVOUS EXCITATION

By CH. S. KOSHTOJANZ, Member of the Academy of Sciences of the Armenian SSR

On the ground of a number of experimental studies, Heilbrunn (1) has advanced the hypothesis that the primary excitation process called forth by the action upon the cell of a stimulant consists in the release on the cellular surface of calcium ions which, as soon as they are liberated from their fixed condition, pass into the protoplasm of the cell (2).

In fact, several writers have reported an appreciable increase of free calcium in muscles upon stimulation and in the eggs of the sea-urchin upon fertilization. Experiments with *Elodea* cells are especially demonstrative. As well known, the protoplasm of these vegetable cells contains a certain amount of ions of oxalic acid. The stimulation of *Elodea* cells with various agents (electrical current, mechanical agents, ultra-violet light, heat, changes of osmotic pressure) leads to the falling out of crystals of calcium oxalate into the stimulated cells. This is a most demonstrative proof of the formation of calcium oxalate crystals; the phenomenon does not set in if the cells have been treated before the stimulation with a solution of oxalates, binding thereby the intracellular reserves of calcium (3).

On the isolated muscle fibres of *m. adductor magnus* of the frog, Heilbrunn (4) showed that the direct action of calcium ions calls forth in these fibres a well-pronounced contraction (1941).

Heilbrunn's cyto-physiological investigations have been repeated by myself on identical material; earlier observations by Chambers and Hale (5) also testify to the high sensitivity of the protoplasm of muscle cells to calcium ions.

It is generally known that the perfusion of sodium oxalate through the vessels of certain muscles deprives the latter of the capacity to respond to direct electric stimulation.

Magnizky and Koshtojanz (unpublished data), working in 1926 with Löwen-Tredelenburg's preparations, have found that when indirect excitability has been abolished by means of sodium oxalate (*i. e.* when the calcium ions are bound), it is almost impossible to restore it.

As pointed out above, in Heilbrunn's experiments the application of sodium oxalate abolished excitability in all cases, irrespective of the stimulants used. Now, from the point of view of the participation in the process of excitation of chemical mediators, the question arises as to the effect which those chemical substances, and more precisely acethylcholine, may produce, when applied to the cell under the conditions of Heilbrunn's experiment.

I have undertaken the experimental analysis of the following question: what will be the mode of reaction of muscle cells in response to acethylcholine, when these cells are under the influence of sodium oxalate, *i. e.* when their calcium ions are bound?

The experiments were carried out in collaboration with R. L. Mitropolitanskaya, in spring 1942, on *m. rectus abdominis* of the frog. The dilution of acethylcholine was $1 \cdot 10^{-6}$. After testing the reaction of the muscle to this solution in Ringer saline, the latter was replaced by an isotonic solution of sodium oxalate. Thereupon the effect of acethylcholine was tested again at various periods of the after-effect of sodium oxalate. After this, the solution containing oxalate was again replaced by Ringer solution containing calcium ions, and the effect of acethylcholine tested anew.

The muscle responds to the isotonic solution of sodium oxalate by irregular, spontaneous contractions resembling those of the skeletal muscle in Biedermann's solution; at this phase the tonus of the muscle is considerably increased. The return to normal Ringer solution leads to the disappearance of these phenomena; however, the spontaneous contractions may also disappear when the action of sodium oxalate is protracted.

Our experiments show that contraction of *m. rectus abdominis* produced by acethylcholine is somewhat attenuated during the first phase of the action of sodium oxalate and vanishes subsequently altogether. If a muscle treated with sodium oxalate and failing to respond to the action of acethylcholine is transferred to Ringer solution again, its normal response to acethylcholine is restored.

It follows from the experiments referred to above that the effect of such a chemical agent as acethylcholine is brought about by the calcium ions, *i. e.* that acethylcholine does not differ in this respect from the physical stimulants studied by Heilbrunn.

On the strength of our earlier studies carried out jointly with Magnizky (1926), of our observations on the action of calcium ions on isolated muscular fibres, made in order to check up Heilbrunn's experiments, and of the experiments with the straight muscle of the abdomen of the frog here described, we consider it probable that the acethylcholine which is released from a fixed state during nerve excitation, does not affect the protoplasm directly, but acts upon it by mobilizing calcium ions, this mobilization consisting in the release of calcium ions from their non-ionized compound with colloids present on the cell's surface.

This hypothesis was advanced by me at the beginning of 1943 at a conference held at the Biochemical Laboratory of J. O. Parnas, Member of the Academy. My assumption was that the liberation of calcium ions from the corresponding compound takes place under the influence of the acetic acid which is formed in the course of hydrolysis of acethylcholine under the action of cholinesterase.

This assumption finds support in the work of Du Bois and Potter ([6]), published in the second half of 1943. On the ground of their biochemical investigations, these authors have also arrived at the conclusion that acethylcholine is a «mediator» of the action of calcium ions.

Du Bois and Potter's experimental data point to the activizing influence of acethylcholine upon the activity of adenosintriphosphotase.

It was further shown by Engelhardt and Lubimova ([7]) that myosin possesses an adenosintriphosphotasic activity and that the decomposition of adenosintriphosphoric acid is a primary chemical reaction yielding the energy for muscular contraction; these facts permit to establish the relationship between acethylcholine and the system myosin—adenosintriphosphoric acid, and to define the chemical system correlating adenosintriphosphoric acid with guanidin-phosporic compounds and with certain stages of glycolysis.

Viewed under this angle, the problem of the action of the chemical agents of the nervous process (so-called mediators of nervous excitation) should be considered in intimate connexion with those enzymic chemical transformations which underly the process of reversible deformation of the contractile elements of muscular protoplasm.

On the ground of the experiments proving the activizing influence of calcium ions upon adenosintriphosphotase ([8], [9]) and of the evidence and considerations in favour of the getting free of calcium ions from the fixed state by acethylcholine (as shown by the abolition of its effect in the absence of these ions), the conclu-

sion can so far be made that muscular contraction, as a response to the action of acethylcholine (or to stimulation of cholinergetic nerves), is connected with the setting free of calcium ions, and consequently with the activation of the enzymic decomposition of adenosintriphosphate, *i. e.* of the first link in the chemical dynamics of muscular protoplasm.

Our data, together with the theoretical treatment of the problem, make it thus possible to give a new interpretation to the «paradoxical» action of acethylcholine upon the heart muscle (relaxation of the muscular tissue).

In the case of heart muscle we suppose the action of acethylcholine to be connected with the magnesium and potassium ions, these ions being known to produce a strong inhibitory influence upon adenosintriphosphotase [Lubimova and Pevsner, 1940, Mehl and Sexton, 1943 ([10])]. It may be assumed that in the action of acethylcholine, or of the stimulation of *n. vagus*, upon the heart, it is magnesium or potassium, rather than calcium, that is involved in the chain of excitatory processes, the inhibitory effect of these ions consisting in the reduction of the decomposition of adenosinpolyphosphates. It is probably this process which is responsible for the so-called «magnesium narcosis» ([7]) leading to relaxation of the cardiac musculature in response to acethylcholine and cholinergic nerves.

Since the liberation of calcium ions (and consequently, the activation of adenosintriphosphotase), brought about by acethylcholine, involves a number of consecutive enzymo-chemical reactions, it should be expected that the rôle of acethylcholine in the process of excitation (*resp.* muscular contraction) is much wider than hitherto supposed. On the one hand, acethylcholine takes part in the exchange of phosphoric groups, *e. g.* by acting directly upon the depots of guanidin-phosphoric compounds, a process promoting the constant regeneration of adenosinpolyphosphates; on the other hand, it acts as a depolarizing agent, in a way which is as yet not quite clear, favouring the onset and conduction of excitation.

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PHYSIOLOGY

MALIGNANT GROWTH IN MAN AS DIAGNOSTICATED BY BLOOD SERUM TOXICITY FOR *PARAMOECIA*

By O. K. NASTIUKOVA

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Introduction. The toxicity of the blood serum of man and animals affected by malignant growth has more than once been tested on *Paramoecia* ([1]—[3]). These studies, however, are marked by a lack of precision in the measuring of the toxic effect. I made use therefore of an improved method worked out at the Laboratory for Ecology of this University, described for the first time by Alpatov and the present author ([4]). With the aid of this method I have succeeded in demonstrating that the serum from the blood of animals affected by malignant tumours produced a toxic effect upon *Paramoecia* ([5]); it has been proved besides that the serum prepared with the blood of rabbits grafted with Brown-Pearce's tumours has a sharply pronounced toxic effect from the very first days of the development of the tumour.

The material used in this work was collected by me in the course of a study carried out in collaboration with Prof. G. Roskin at the Laboratory for Morphology of the Institute of Physiology of the Academy of Sciences of the USSR (head Prof. G. Roskin). The results obtained have already been described in a preliminary note ([6]). The present article contains the result of a more thorough statistical treatment of the material. I feel it my pleasant duty to express my gratitude to Prof. F. M. Lampert for his most valuable help in collecting the clinical material, and to Prof. W. W. Alpatov, for many a helpful advices in the course of the biometrical treatment of the data obtained.

Method. The blood taken from the ulnar vein was centrifuged, and the serum obtained diluted with boiled tap-water. One drop of the serum was diluted in one, two or three cm^3 of water; in this way media were obtained with a serum concentration of 1.25, 1.85 and 3.70 per cent, respectively. The medium was poured over 16—20 hollow slides, 5 drops over each hole, and one *Paramoecium caudatum* from a hay culture was placed on to each hole. The glasses with the infusoriae were transferred to humid chambers, in large Petri dishes with moist filter-paper, which in their turn were placed in a common humid chamber and afterwards in a thermostat at 25° C. After 24 hours records were made of the number of *Paramoecia* in the holes.

Material. Serum of 79 diseased and 13 healthy human subjects was tested. The clinical material was obtained at the Blagushinsky Hospital, Moscow.

The cases investigated were distributed into the following groups: 1) 34 cancer cases, with diagnosis confirmed by patho-anatomical examination; 2) 13 cancer cases, with clinical diagnosis only; 3) 7 patients with benign tumours confirmed by patho-anatomical examination; 4) 5 patients with benign tumors subjected to no patho-anatomical examination; 5) 2 patients with tumours of undefined nature; 6) 2 echinococcus cases; 7) 5 patients suffering from stomach

ulcer and gastritis; 8) 4 cases of femur fractures and post-operational regeneration processes; 9) 2 tubercular patients; 10) 2 cases of Basedow's disease; 11) 3 pregnancy cases; 12) 10 patients upon removal of cancerous tumours, six of them examined before operation, as well.

Results. The data obtained were treated in the following manner: for each patient there was calculated the absolute vital index of *Paramoecia* which had passed 24 hours in a serum of a definite concentration. The index was calculated after the formula: $i\,\% = \frac{N_2}{N_1}$, where N_1 is the number of *Paramoecia* placed in the glass-holes, and N_2, the number of *Paramoecia* found there after 24 hours. The relative vital index was calculated after the formula $i\,\% = \frac{N_2 - N_c}{N_c} 100$, where N_c is the number of infusoriae after 24 hours in a medium added with serum of healthy human subjects, at the condition that the number of infusoriae placed for propagation into control and experimental sera be equal.

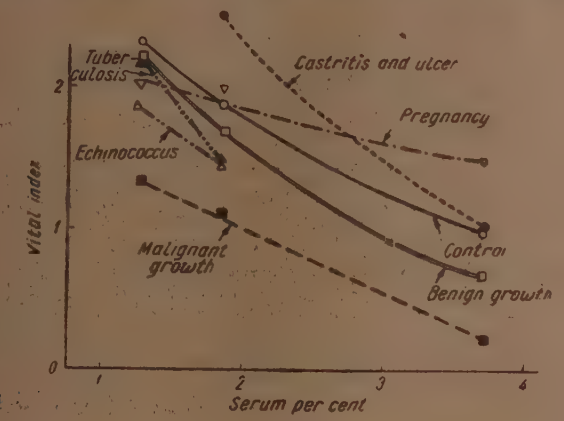

Fig. 1

Fig. 1 represents curves of toxicity according to mean indices obtained from patients with both clinical and patho-anatomical diagnosis.

From these curves it is evident that the *Paramoecia* show a much lower vitality in a medium added with serum of the blood of cancerous patients than with that of healthy human subjects. Benign tumours give a curve passing near that of healthy human subjects, the vital activity of the *Paramoecia* being but slightly suppressed.

Table 1

Arithmetical Means (M) and Mean Errors ($\pm m$) in Vitality Index of *Paramoecia*

	Concentration of serum, in per cent		
	1.25	1.85	3.7
Healthy subjects	2.29 ± 0.194	1.85 ± 0.149	1.01 ± 0.227
Number of cases	9	13	7
With benign tumours	2.18 ± 0.196	1.67 ± 0.118	0.65 ± 0.129
Number of cases	3	7	4
With malignant tumours	1.33 ± 0.121	1.07 ± 0.127	0.23 ± 0.082
Number of cases	20	34	14
Upon removal of malignant tumour	1.78	1.58 ± 0.247	0.74 ± 0.156
Number of cases	1	10	9

The toxicity curves of patients suffering from gastritis, ulcers, tuberculosis and those of pregnant women show that all these conditions give some deviations from the normal, though no essential ones.

In order to estimate the significance of the means obtained, the individual indices were subjected to a biometrical treatment. The constants derived are given in Tables 1 and 2.

From these data it may be inferred (Table 2) that the difference between the blood toxicity of 1) healthy human subjects and cancerous patients, and 2) between patients with benign tumours and cancerous patients, is statistically signi-

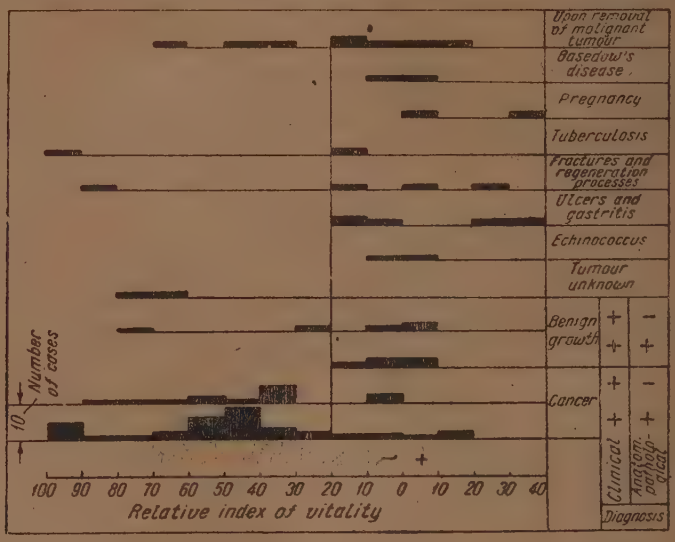

Fig. 2

ficant for all serum concentrations, since R exceeds 3, or approaches it very closely (R=Diff : m_{Diff}).

Table 2

Significance Index of Difference Between Vitality of Healthy and Diseased Subjects

	Concentration of serum, in per cent		
	1.25	1.85	3.7
Healthy subjects and cancerous patients	+ 4.23	+ 3.99	+ 3.23
Healthy subjects and patients upon removal of malignant tumour	+ 0.95	+ 1.03	+ 0.8?
Healthy subjects and patients with benign tumours	+ 0.4	+ 0.95	+ 1.38
Patients with benign tumours and cancerous patients	+ 3.71	+ 3.47	+ 2.78
Patients before and after removal of cancerous tumours	—	— 2.03	— 2.9

The differences are not significant in the case of comparison of the toxicity of the serum of healthy subjects with that of patients upon operation, and also in the case where the serum of healthy subjects is compared with that of patient affected with benign growth. Operated cancerous patients show a reduced blood toxicity.

However, for the concentration of 1.85 per cent the differences obtained exceed their mean error 2.03 times only, the probability of this difference being not due to errors of random sampling, but being equal to 21 against unity.

The sensitivity of *Paramoecia* to toxical substances varies within a rather wide range, this variation being dependent on a number of circumstances (age of the culture, strain, hour of the day, season, *etc.*). It has therefore been decided to determine the relative vital index of the *Paramoecia* for all the patients investigated in order to show the individual variation in the serum toxicity.

Fig. 2 shows the histograms of the index for all the cases investigated; the concentration of the serum applied was 1.85 per cent. It may be seen that the vast majority of cancerous cases are characterized by a relative vital index shifted to the left of the point corresponding to minus 20 per cent. Patients of other groups pass this limit only as rare exceptions. Let us cite some of those exceptional cases. One of the patients who was supposed to have a benign tumour (there has heen no patho-anatomical diagnosis, and since clinical diagnosis was questionable in this case, as a matter of fact we may deal here with a cancerous patient); in two cases there were neoformations of undefined nature; in one case, a regeneration process; and lastly, there was one case of tuberculosis which is also rather doubtful, since the patient had on his neck a tbc tumour which had originally been diagnosticated as a lymphadenoma.

Table 3

Indices of Relative Vitality of *Paramoecia* from Cultures Grown on Sera of Patients before and after Removal of Malignant Tumours

Nos.	Before operation				After operation					Diagnosis
	date of serum testing	serum concentr., %			date of operation	date of serum testing	serum concentr., %			
		1.25	1.85	3.7			1.25	1.85	3.7	
1	2.XI	—	—39.8	— 72.3	4.XI	27.XI	—	— 0.00	+ 5.9	*cr. mammae*
2	2.XII	—	—43.8	—100.0	10.XII	27.XII	—	—17.9	— 12.5	» »
3	20.II	—29.7	—44.9	—	21.II	8.III	—4.8	—16.7	— 5.9	» »
4	8.III	—	—32.4	— 88.3	19.III	21.III	—	—37.5	— 61.5	» »
						31.III	—	—34.4	—100.0	
5	21.III	—	— 9.4	+ 15.3	22.III	31.III	—	—11.8	— 57.2	Relapse of thigh sarcoma
6	31.III	—	—87.5	— 61.3	1.IV	7.IV	—	— 6.25	—14.8	*cr. mammae*

The variation of the vital index of *Paramoecia*, as brought out in Table 3, testifies to a drop in the blood serum toxicity of cancerous patients after operation. In a single case out of five only (No. 4) no decrease in toxicity could be noted.

This exception may possibly be accounted for by an incomplete removal of the tumour, or by the presence of metastases in some other organ.

Discussion of Results and Conclusions. The blood of patients affected by cancerous growth has been found to contain a toxine which disappears as soon as the tumour has been removed, and is scarcely ever observed in other diseases. It seems of interest to compare this toxine whose effect is to suppress the multiplication of infusoriae and to kill them, with the gaseous toxine suppressing the budding of yeast (7), as well as with the «extinguisher» of the mitogenetic radiation of the blood, which was discovered by Siebert in 1937. At the time being we have no data to discuss the nature of this toxine. The clear-cut quantitative characteristic of the toxicity of blood serum, which we succeeded to obtain using *Paramoecia* as test-objects, permits of suggesting this method for the diagnostication of malignant growth. If we are to assume that the blood of cancerous patients is characterized by a relative vital index of —20 per cent and above (according to the absolute value of the index), then from the histogram of Fig. 2 it may be inferred that the reaction for cancer gives a positive answer in 85 per cent of the cases of malignant growth, in 0 per cent of benign tumours

(established by patho-anatomical diagnosis), and in 11.1 per cent of various diseases and pregnancy.

Let us compare these data with those of the five most successful cancer reactions, as obtained by Martynova ([8]); with cancerous patients these five reactions give a positive response in 95.9; 90.8; 84.7; 74.8 and 71 per cent of cases, respectively. In other words, the *Paramoecia* reaction may claim to the third place as to the success of diagnostication. It is also necessary to compare this reaction with the five reactions for cancer approved by Martynova because of the response on the part of non-cancerous patients to these reactions. Let us list them: Kahn's reaction, albumen reaction, Lange's reaction, Davis' reaction and that of Kopachevsky. All these reactions give a positive answer with non-cancerous patients in 30.1—34.8 per cent of cases, whereas the *Paramoecia* reaction gives on the average $(11.1+0):2=5.5$ per cent of positive answers (the group of benign tumours being united with that of other diseases).

The diagnostication of cancer by the disappearance of the mitogenetic radiation of the blood ([9]), as applied by different experimenters, yields from 70 to 100 per cent of positive answers coinciding with the actual existence of cancerous growth ([10]).

All this gives us ground to believe that the *Paramoecium* reaction deserves to be introduced into the clinical laboratory practice.

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